



STATEMENT

I, Yasuhide KOBAYASHI hereby state that I have a thorough knowledge of the English and Japanese languages and that the attached document is an accurate English translation of the Priority document of Japanese Patent Application No. 2003-434142 filed on December 26, 2003, upon which the present application claims a priority.

Declared at Tokyo, Japan

This 1st day of December, 2010

A handwritten signature in black ink, consisting of several fluid, connected strokes.

Yasuhide Kobayashi



PATENT OFFICE
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This is to certify that the annexed is a true copy of the following application as filed with this Office.

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(Article) Specification 1 copy

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[Document Type] Claims

[Claim 1]

An antireflection film including hollow silica particles and a compound lowering a surface free energy in a low-refractive index layer, wherein the low-refractive index layer is located at the furthest position from a transparent support.

[Claim 2]

The antireflection film according to claim 1, wherein the compound lowering the surface free energy has at least one selected from the group consisting of a silicone compound and a fluorine-containing compound.

[Claim 3]

The antireflection film according to claim 2, wherein the compound capable of lowering the surface free energy is the silicone compound.

[Claim 4]

The antireflection film according to any one of claims 1 to 3, wherein the compound lowering the surface free energy includes at least one group having reactivity with a binder in molecules.

[Claim 5]

The antireflection film according to any one of claims 1 to 4, wherein the compound lowering the surface free energy includes at least one active energy ray-curable (meth)acryloyl group in its molecules.

[Claim 6]

An antireflection film including hollow silica particles and a binder capable of lowering the surface free energy in a low-refractive index layer, wherein the low-refractive index layer is located at the furthest position from a transparent support.

[Claim 7]

The antireflection film according to any one of claims 1 to 6, wherein a silicone and/or a fluoroalkyl group is segregated at a surface of the low-refractive index layer such that a photoelectric spectral intensity ratio Si/C and/or F/C in the uppermost surface and a lower layer located at 80 % of the distance from the uppermost surface of the low-refractive index layer is larger by at least 5 times than that of the 80 % lower layer in the uppermost surface.

[Claim 8]

The antireflection film according to claims 6 or 7, which includes the binder capable of lowering the surface free energy in a low-refractive index layer, and the binder including the silicon and/or a fluorine, wherein the low-refractive index layer is located at the furthest position from a transparent support.

[Claim 9]

The antireflection film according to any one of claims 6 to 8, wherein the binder capable of lowering the surface free energy is a fluorine-containing polymer.

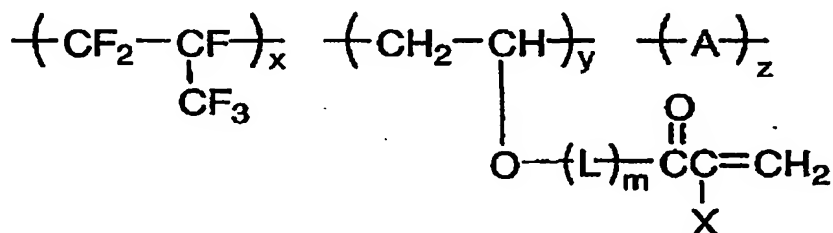
[Claim 10]

The antireflection film according to any one of claims 6 to 9, wherein the binder capable of lowering the surface free energy is a compound including at least one active energy ray-curable (meth)acryloyl group.

[Claim 11]

The antireflection film according to any of claims 6 to 10, wherein the binder is represented by formula (1):

Formula (1)



wherein L represents a linking group having from 1 to 10 carbon atoms; m represents 0 or 1; X represents a hydrogen atom or a methyl group; A represents a repetitive unit derived from a vinyl monomer; x, y and z each indicates mol% of the respective constituent, and satisfy $30 \leq x \leq 60$, $5 \leq y \leq 70$ and $0 \leq z \leq 65$.

[Claim 12]

The antireflection film according to any one of claims 1 to 11, wherein the surface free energy is 25 mN/m or less.

[Claim 13]

The antireflection film according to any of claims 1 to 12, which includes a layer including at least one of a hydrolysate of an organosilane and a partial condensate of

the organosilane in at least one of a low reflective index layer located at the furthest position from a support and a lower layer of the low reflective index layer, wherein the hydrolysate and the partial condensate is produced in the presence of at least one of an acid catalyst and/or a metal chelate compound, and the organosilane is represented by formula (A):



(wherein R^{10} represents a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; X represents a hydroxyl group or a hydrolyzable group; and m indicates an integer of 1 to 3.)

[Document Type] Specification

[Title of the Invention] ANTIREFLECTION FILM, POLARIZING PLATE, AND LIQUID CRYSTAL DISPLAY DEVICE

[Technical Field of the Invention]

[0001]

The invention relates to an antireflection film, a polarizing plate and an image display device using the same.

[Background Art]

[0002]

In general, in image display devices such as cathode-ray tube display devices (CRT), plasma display panels (PDP), and liquid crystal display devices (LCD), an antireflection film is disposed on the outermost surface of the display which reduces reflectivity by using the principle of optical interference for preventing contrast reduction or image reflection.

[0003]

In order to reduce reflectivity in the antireflection film, a low-refractive index layer has to have a substantially lowered refractive index. As a material for lowering the refractive index, magnesium fluoride and calcium fluoride are exemplified as inorganic substances, and fluorine-containing compounds having a large fluorine-containing ratio are exemplified as organic substances. However, since these fluorine compounds do not have cohesion force, as a film disposed on the outermost surface of the

display, the scratch resistance is not satisfactory. Further, it is necessary that stain resistance is provided by the film since the film is disposed on the outermost surface, but it was difficult to obtain good stain resistance using only technique such as disclosed in Patent Document 1 (JP-A-2002-265866) and Patent Document 2 (JP-A-2002-317152). Thus, in order to simultaneously lower reflection, satisfy good scratch resistance and stain resistance, so-called low surface free energy compound having a low refractive index, excellent strength, and where stains are difficult to attach to the surface, was necessary. In many cases, there is a trade-off relationship that if one is improved then other one is worsen, it was difficult to satisfy any one of reflectivity lowering, scratch resistance and stain resistance.

[0004]

For the intended reflective index reduction, Patent Document 3 (JP-A-7-287102) discloses a technique of increasing the refractive index of a hard-coat layer to thereby reduce the refractive index. However, color heterogeneity occurs in such a high-refractive index hard-coat layer since the refractive index difference between the layer and the support is large, and the wavelength dependency of the refractive index of the film greatly varies.

[0005]

Patent Document 4 (JP-A-7-333404) describes an

antiglare-antireflection film having good gas-barrier properties, antiglare properties and antireflection properties. However, since this requires a silicone oxide film to be formed by CVD, its productivity is low when compared with wet-coated films.

[Patent Document 1] JP-A-2002-265866

[Patent Document 2] JP-A-2002-317152

[Patent Document 3] JP-A-H7-287102

[Patent Document 4] JP-A-H7-333404

[Disclosure of the Invention]

[[Problem to be Solved by the Invention]

[0006]

An object of the invention is to provide an antireflection film that is easily and inexpensively producible and that has a good antireflection capability, good scratch resistance, and good stain resistance.

Another object of the invention is to provide a polarizing plate and a liquid crystal display device utilizing the antireflection film of such excellent ability.

[Means for Solving the Problem]

[0007]

According to the invention, there are provided an antireflection film having the constitution mentioned below, a polarizing plate and a liquid crystal display device, and the above-mentioned objects are attained by these.

1. An antireflection film including hollow silica particles and a compound lowering a surface free energy in a low-refractive index layer, wherein the low-refractive index layer is located at the furthest position from a transparent support.
2. The antireflection film according to the above 1, wherein the compound lowering the surface free energy has at least one type selected from the group consisting of a silicone compound and a fluorine-containing compound.
3. The antireflection film according to the above 2, wherein the compound capable of lowering the surface free energy is the silicone compound.
4. The antireflection film according to any one of the above 1 to 3, wherein the compound lowering the surface free energy includes at least one group having reactivity with a binder in its molecules.
5. The antireflection film according to any one of the above 1 to 4, wherein the compound lowering the surface free energy includes at least one of active energy ray-curable (meth)acryloyl group in its molecules.
6. An antireflection film including hollow silica particles and a binder capable of lowering the surface free energy in a low-refractive index layer, wherein the low-refractive index layer is located at the furthest position from a transparent support.
7. The antireflection film according to any one of the above

1 to 6, wherein a silicone and/or a fluoroalkyl group is segregated at an surface of the low-refractive index layer such that a photoelectric spectral intensity ratio Si/C and/or F/C in the uppermost surface and a lower layer located at 80 % of the distance from the uppermost surface of the low-refractive index layer is larger by at least 5 times than that of the 80 % lower layer in the uppermost surface.

8. The antireflection film according to the above 6 or 7, which includes the binder capable of lowering the surface free energy in a low-refractive index layer, and the binder including the silicon and/or a fluorine, wherein the low-refractive index layer is located at the furthest position from a transparent support.

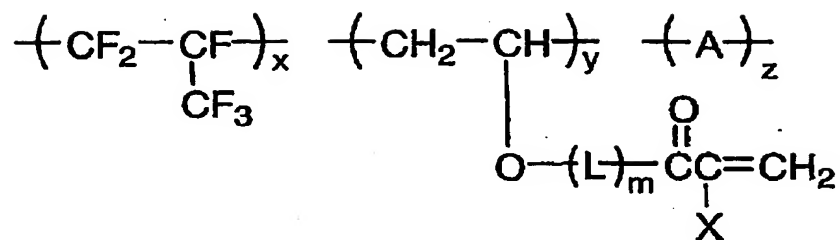
9. The antireflection film according to any one of the above 6 to 8, wherein the binder capable of lowering the surface free energy is a fluorine-containing polymer.

10. The antireflection film according to any one of the above 6 to 9, wherein the binder capable of lowering the surface free energy is a compound including at least one of active energy ray-curable (meth)acryloyl group.

11. The antireflection film according to any of the above 6 to 10, wherein the binder is represented by formula (1):

[0008]

Formula (1)



[0009]

(In formula, L represents a linking group having from 1 to 10 carbon atoms; m represents 0 or 1; X represents a hydrogen atom or a methyl group; A represents a repetitive unit derived from an arbitrary vinyl monomer; x, y and z each indicates mol% of the respective constituent, and satisfy $30 \leq x \leq 60$, $5 \leq y \leq 70$ and $0 \leq z \leq 65$.)

[0010]

12. The antireflection film according to any one of the above 1 to 11, wherein the surface free energy is 25 mN/m or less.

13. The antireflection film according to any of the above 1 to 12, which includes a layer including at least one of a hydrolysate of an organosilane and a partial condensate of the organosilane in at least one of a low reflective index layer located at the furthest position from a support and a lower layer of the low reflective index layer, wherein the hydrolysate and the partial condensate is produced in the presence of at least one of an acid catalyst and a metal chelate compound, and the organosilane is represented by formula (A):

Formula (A): $(R^{10})_m\text{Si}(X)_{4-m}$

(In formula, R^{10} represents a substituted or unsubstituted

alkyl group, or a substituted or unsubstituted aryl group; X represents a hydroxyl group or a hydrolyzable group; and m indicates an integer of 1 to 3.)

14. A polarizing plate including an antireflection film according to any one of the above 1 to 13.

15. A liquid crystal display device including an antireflection film according to any one of the above 1 to 13, or a polarizing plate according to the above 14.

[Effect of the Invention]

[0011]

The antireflection film of the invention can be produced in a simplified manner and inexpensively, and has good antireflection capability, scratch resistance and stain resistance.

Further, the invention provides a polarizing plate provided with the above-mentioned antireflection film of the invention. The liquid crystal display device of the invention that is provided with the antireflection film or the polarizing plate has good visibility and has good scratch resistance and stain resistance since the antireflection film is disposed on the outermost surface.

[Best Mode for carrying out the Invention]

[0012]

The basic constitution of one preferred aspect of the antireflection film of the invention is described with

reference to the drawing.

Fig. 1 is a schematic cross-sectional view graphically showing one example of the antireflection film of the invention. In this case, the antireflection film 1 has a layer constitution of a transparent support 2, a conductive layer 3, a hard-coat layer 4, a middle-refractive index layer 5, a high-refractive index layer 6 and a low-refractive index layer 7 superposed in this order. The middle-refractive index layer 5 and the high-refractive index layer 6 are optional layers that may be present or absent in the layer constitution, and the hard-coat layer 4 may optionally contain mat particles 8 or may not. Preferably, the refractive index of the hard-coat layer 4 is in the range from 1.50 to 2.00, and the refractive index of the low-refractive index layer 7 is in the range from 1.38 to 1.49. When the high-refractive index layer 6 and the middle-refractive index layer 5 are used, their refractive index may satisfy the condition of "refractive index of low-refractive index layer 7 < refractive index of middle-refractive index layer 5 < refractive index of high-refractive index layer 6". Though not indispensable, the conductive layer 3 is preferably in the layer constitution. It may not be between the transparent support 2 and the hard-coat layer 4, but may be in any position in the constitution of the antireflection film. The conductive layer 3 may be integrated with any layer in the layer constitution. In this specification, when

the numerical data indicate physical data or characteristic data, then the expression for them "a number to another number (or from a number to another number)" means the range that falls between the former number and the latter number both inclusive.

[0013]

[Low-refractive index layer]

First described is the low-refractive index layer in the invention.

A refractive index of the low-refractive index layer in the antireflection film of the invention is in the range of 1.38 to 1.49, preferably range of 1.38 to 1.44. The low-refractive index layer satisfies the following formula (I) from the viewpoint of reducing the reflectivity of the layer.

$$(I) \quad (m\lambda/4) \times 0.7 < n_1 d_1 < (m\lambda/4) \times 1.3$$

wherein m is a positive odd number; n_1 is a refractive index of the low-refractive index layer; d_1 is a thickness (nm) of the low-refractive index layer; and λ is a wavelength falling between 500 and 550 nm. Satisfying formula (I) means the presence of m (this is a positive odd number, and is generally 1) that satisfies formula (I) within the above-mentioned wavelength range.

[0014]

The invention includes hollow silica particles and a compound lowering the surface free energy in the low-refractive index layer.

The hollow silicon particles included in the low-refractive index layer of the invention is described below.

The refractive index of the hollow silicon particle is preferably from 1.17 to 1.40, more preferably from 1.17 to 1.35, most preferably from 1.17 to 1.30. The refractive index as referred to herein means the refractive index of the entire particle. Therefore, the refractive index does not mean the refractive index only of the silica in the shell where the hollow silica particles is formed. In this case, when the radius of the hollow within the particle is represented by "a" and the radius of the particle shell is by "b", then the porosity "x" to be represented by the following formula (I) is preferably from 10 to 60 %, more preferably from 20 to 60 %, most preferably from 30 to 60 %.

$$(I) \quad x = (4\pi a^3/3)/(4\pi b^3/3) \times 100$$

When the refractive index of the hollow silica particles is further lowered and the porosity thereof is further increased, then the thickness of the shell may be thin and the strength of the particles may be low. Therefore, from the viewpoint of the scratch resistance thereof, low-refractive index particle having a refractive index of lower than 1.17 are impracticable. The refractive index of the hollow silica particles is determined with an Abbe's refractometer (made by Atago Co., Ltd.). Methods for producing hollow silica are described, for example, in JP-A-2001-233611 and JP-A-2002-79616.

[0015]

From the viewpoint of effect of lowering the refractive index or improving the scratch resistance, and from the view point of the integrated reflectivity or the appearance such as black compaction and the like, the coating amount of the hollow silica is preferably from 1 mg/m^2 to 100 mg/m^2 , more preferably from 5 mg/m^2 to 80 mg/m^2 , even more preferably from 10 mg/m^2 to 60 mg/m^2 . The mean particle size of the hollow silica is preferably from 30 % to 150 %, more preferably from 35 % to 80 %, even more preferably from 40 % to 60 % of the thickness of the low-refractive index layer. Accordingly, when the thickness of the low-refractive index layer is 100 nm, then the particle size of the hollow silica is preferably from 30 nm to 150 nm, more preferably from 35 nm to 80 nm, even more preferably from 40 nm to 60 nm.

When the particle size of the hollow silica falls within the range as above, then the fraction of the porosity portion is to be appropriate and the refractive index is lowered, further, fine protrusions formed on the surface of the low-refractive index layer is prevented. Thus, there are no deteriorations of the integrated reflection or the appearance such as black compaction.

The fine silica particle may be crystalline or amorphous. It is preferably monodispersed particle. Regarding morphology, it is most preferably spherical, but may be amorphous with no problem. The mean particle size of

the hollow silica may be determined on electromicroscopic photographs.

[0016]

In the invention, hollowless silica may be used along with the hollow silica particles. The particle size of the silica particle without hollowness is preferably from 30 nm to 150 nm, more preferably from 35 nm to 80 nm, most preferably from 40 nm to 60 nm. Preferably, at least one type of fine silica particles having an mean particle size of less than 25 % of the thickness of the low-refractive index layer (this is referred to as "a small-size fine silica particle") is combined with the silica particles having the above-mentioned particle size (this is referred to as "a large-size fine silica particle"). Since small-size fine silica particles may exist in the spaces between the large-size fine silica particles, they may serve as a fixer for the large-size fine silica particles. The mean particle size of the small-size fine silica particle is preferably from 1 nm to 20 nm, more preferably from 5 nm to 15 nm, even more preferably from 10 nm to 15 nm. Using the fine silica particle of the type is preferred in point of the cost of the materials and of the effect of the particles as fixer.

[0017]

The above-mentioned fine silica particles may be processed for physical surface treatment such as plasma discharge treatment or corona discharge treatment, or for

chemical surface treatment with surfactant or coupling agent, in order to ensure their dispersion stability in dispersions or coating liquids or in order to enhance their affinity and bonding ability to binder components. More preferably, coupling agent is used for the treatment. The coupling agent is preferably an alkoxymetal compound (e.g., titanium coupling agent, silane coupling agent). Above all, treatment with a silane coupling agent having an acryloyl group or a methacryloyl group is especially effective. The above-mentioned coupling agent is used for surface treatment as a surface-treating agent for inorganic filler in the low-refractive index layer before a coating liquid for the layer is prepared, but it is preferably added to the coating liquid for the layer as an additive thereto while the coating liquid is prepared, and it is thereby added to the layer. Preferably, silica fine particles are previously dispersed in medium before a surface treatment for reducing the load of surface treatment.

Within scope for accomplishing the objective of the invention, other fine particles such as magnesium fluoride than fine silica particles may be added along with the hollow silica particles into low-refractive index layer.

[0018]

With reference to D.K. Owens, J. Appl. Polym. Sci., 13, 1741 (1969), the surface free energy (γ_s^v : unit, mN/m) of the antireflection film of the invention is defined by the

surface tension of the antireflection film that is calculated as the value γ_s^v ($=\gamma_s^d+\gamma_s^h$), or that is, the sum of γ_s^d and γ_s^h obtained according to the following simultaneous equations (1) and (2) from the contact angles θ_{H_2O} and $\theta_{CH_2I_2}$ of pure water H_2O and methylene iodide CH_2I_2 experimentally determined on the antireflection film. When γ_s^v is smaller and the surface free energy is lower, then the film surface has high repellency and therefore has good stain resistance. Preferably, the surface free energy of the antireflection film is preferably at most 25 mN/m, more preferably at most 20 mN/m.

$$(1) \quad 1+\cos\theta_{H_2O} = 2\sqrt{\gamma_s^d}(\sqrt{\gamma_{H_2O}^d}/\gamma_{H_2O}^v) + 2\sqrt{\gamma_s^h}(\sqrt{\gamma_{H_2O}^h}/\gamma_{H_2O}^v)$$

$$(2) \quad 1+\cos\theta_{CH_2I_2} = 2\sqrt{\gamma_s^d}(\sqrt{\gamma_{CH_2I_2}^d}/\gamma_{CH_2I_2}^v) + 2\sqrt{\gamma_s^h}(\sqrt{\gamma_{CH_2I_2}^h}/\gamma_{CH_2I_2}^v)$$

* $\gamma_{H_2O}^d = 21.8$, $\gamma_{H_2O}^h = 51.0$, $\gamma_{H_2O}^v = 72.8$, $\gamma_{CH_2I_2}^d = 49.5$, $\gamma_{CH_2I_2}^h = 1.3$, $\gamma_{CH_2I_2}^v = 50.8$. After the antireflection film has been conditioned at 25°C and 60 % RH for at least 1 hour, the contact angle on it is measured under the same condition as that for the preconditioning.

[0019]

The compound reducing a surface free energy and the binder capable of reducing a surface free energy for use in the invention may be any one, not limited in point of the structure and the composition thereof, so far as it is effective for significantly lowering the surface free energy defined above of the antireflection film when the respective compound is applied to the film. In general, the surface

free energy depression is not linear relative to the amount of the compound applied to the film, and it may be saturated with the increase in the amount thereof. For example, in a surface free energy depression profile curve prepared by plotting the surface free energy depression points relative to the amount of a cured matrix formed of a binder such as DPHA, the surface free energy depression relative to the amount of the compound added to the surface free energy depression saturation point is preferably at least 10 mN/m, more preferably at least 20 mN/m, even more preferably at least 25 mN/m, most preferably at least 30 mN/m.

[0020]

The surface free energy lowering compound may be any of known silicone compounds or fluorine-containing compounds. Preferably, the amount of the compound to be added to the low-refractive index layer is from 0.01 to 20 % by weight of the overall solid content of the layer, more preferably from 0.05 to 10 % by weight, even more preferably from 0.1 to 5 % by weight.

[0021]

Preferred examples of the silicone compound are those having a substituent at least in any of terminals and/or side branches of a compound chain that contains multiple dimethylsilyloxy units as repetitive units. The compound chain containing repetitive dimethylsilyloxy units may contain any other structural unit than dimethylsilyloxy units.

Preferably, the compound contains multiple substituents that may be the same or different. Examples of preferred substituents are those containing any of an acryloyl group, a methacryloyl group, a vinyl group, an aryl group, a cinnamoyl group, an epoxy group, an oxetanyl group, a hydroxyl group, a fluoroalkyl group, a polyoxyalkylene group, a carboxyl group, and amino group. Although not specifically limited, the molecular weight of the compound is preferably at most 100,000, more preferably at most 50,000, even more preferably from 3,000 to 30,000, and most preferably from 10,000 to 20,000. Also not specifically limited, the silicone atom content of the silicone compound is preferably at least 18.0 % by weight, more preferably from 25.0 to 37.8 % by weight, most preferably from 30.0 to 37.0 % by weight. Examples of the preferred silicone compounds are Shin-etsu Chemical's X-22-174DX, X-22-2426, X-22-164B, X22-164C, X-22-170DX, X-22-176D, X-22-1821 (all trade names), Chisso's FM-0725, FM-7725, FM-4421, FM-5521, FM-6621, FM-1121, and Gelest's DMS-U22, RMS-033, RMS-083, UMS-182, DMS-H21, DMS-H31, HMS-301, FMS121, FMS123, FMS131, FMS141, FMS221 (all trade names), to which, however, the invention is not limited.

[0022]

The fluorine-containing compound is preferably a fluoroalkyl group-containing compound. Preferably, the fluoroalkyl group has from 1 to 20 carbon atoms, more preferably from 1 to 10 carbon atoms, and it may have a

linear structure (e.g., $-\text{CF}_2\text{CF}_3$, $-\text{CH}_2(\text{CF}_2)_4\text{H}$, $-\text{CH}_2(\text{CF}_2)_8\text{CF}_3$, $-\text{CH}_2\text{CH}_2(\text{CF}_2)_4$), or a branched structure (e.g., $\text{CH}(\text{CF}_3)_2$, $\text{CH}_2\text{CF}(\text{CF}_3)_2$, $\text{CH}(\text{CH}_3)\text{CF}_2\text{CF}_3$, $\text{CH}(\text{CH}_3)(\text{CF}_2)_5\text{CF}_2\text{H}$), or an alicyclic structure (preferably 5-membered or 6-membered, e.g., a perfluorocyclohexyl group, a perfluorocyclopentyl group, or an alkyl group substituted with any of these); or it may have an ether bond (e.g., $\text{CH}_2\text{OCH}_2\text{CF}_2\text{CF}_3$, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_4\text{F}_8\text{H}$, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$, $\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{H}$). The multiple fluoroalkyl groups may be included in the same molecule.

Preferably, the fluorine-containing compound contains a substituent that contributes to the formation of a bond to the film of the low-refractive index layer or to the compatibility with the film. Also preferably, the compound has multiple substituents, which may be of the same or different type. Examples of the preferred substituent are an acryloyl group, a methacryloyl group, a vinyl group, an aryl group, a cinnamoyl group, an epoxy group, an oxetanyl group, a hydroxyl group, a polyoxyalkylene group, a carboxyl group, and an amino group. The fluorine-containing compound may be a polymer or an oligomer with a compound not containing a fluorine atom, and its molecular weight is not specifically limited. Also not specifically limited, the fluorine atom content of the fluorine-containing compound is preferably at least 20 % by weight, more preferably from 30 to 70 % by weight, most preferably from 40 to 70 % by weight. Examples of the preferred fluorine-containing compound are Daikin's R-

2020, M-2020, R-3833, M-3833 (all trade names), Dai-Nippon Ink's Megafac F-171, F-172, F-179A, Diffenser MCF-300 (all trade names), to which, however, the invention is not limited.

[0023]

The surface free energy lowering compound preferably has at least one group reactive with the binder in the molecule. Examples of the preferred reactive group are thermosetting active hydrogen atom, hydroxyl group, melamine, active energy ray-curable (meth)acryloyl group and epoxy group. Of those, especially melamine or (meth)acryloyl group is preferred.

[0024]

A dust inhibitor and antistatic agent, such as known cationic surfactant or polyoxyalkylene compound may be added to the layer for applying dust-proof and antistatic properties to the layer. The silicone compound and the fluorine-containing compound may contain the structural units of the dust inhibitor and the antistatic agent as a part of their functions. When these are added to the layer as additives, then their amount is preferably from 0.01 to 20 % by weight, more preferably from 0.05 to 10 % by weight, even more preferably from 0.1 to 5 % by weight of the overall solid content of the low-refractive index layer. Examples of the preferred compound are Dai-Nippon Ink's Megafac F-150 (trade name) and Toray-Dow Corning's SH-3748 (trade name), to which, however, the invention is not limited.

[0025]

The binder that may be in the low-refractive index layer of the antireflection film of the invention is described. The binder is preferably a polymer having a saturated hydrocarbon chain or a polyether chain as the backbone structure thereof, more preferably a polymer having a saturated hydrocarbon chain as the backbone structure thereof. Also preferably, the binder polymer has a crosslinked structure.

[0026]

The binder polymer having a saturated hydrocarbon chain as the backbone structure is preferably a polymer of an ethylenic unsaturated monomer. The binder polymer having a saturated hydrocarbon chain as the backbone structure and having a crosslinked structure is preferably a (co)polymer of a monomer having two or more ethylenic unsaturated groups.

[0027]

The monomer having two or more ethylenic unsaturated groups includes esters of polyalcohols and (meth)acrylic acids (e.g., ethylene glycol di(meth)acrylate, 1,4-cyclohexane diacrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,2,3-cyclohexane tetramethacrylate, polyurethane

polyacrylate, polyester polyacrylate), vinylbenzene and its derivatives (e.g., 1,4-divinylbenzene, 4-vinylbenzoic acid-2-acryloylethylester, 1,4-divinylcyclohexanone), vinyl sulfones (e.g., divinyl sulfone), acrylamides (e.g., methylenebisacrylamide), and methacrylamides. Two or more of these monomers may be used as combined. In this description, "(meth)acrylate" indicates "acrylate or methacrylate".

[0028]

Polymerization of these ethylenic unsaturated group-having monomers may be effected through exposure to active energy rays or to heat in the presence of an optical radical initiator or a thermal radical initiator. Accordingly, a coating liquid including an ethylenic unsaturated group-having monomer, an optical radical initiator or a thermal radical initiator, a mat particles and an inorganic filler is prepared, and the coating liquid is applied onto a transparent support, and then polymerized and cured through exposure to active energy rays or to heat to form an antireflection film.

[0029]

The optical radical initiator includes acetophenones, benzoin, benzophenones, phosphine oxides, ketals, anthraquinones, thioxanthenes, azo compounds, peroxides, 2,3-dialkyldione compounds, disulfide compounds, fluoroamine compounds, and aromatic sulfoniums. Examples of acetophenones are 2,2-diethoxyacetophenone, p-

dimethylacetophenone, 1-hydroxydimethylphenyl ketone, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-4-methylthio-2-morpholinopropiophenone, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone. Examples of benzoin benzenesulfonic acid ester, benzoin toluenesulfonic acid ester, benzoin methyl ether, benzoin ethyl ether, and benzoin isopropyl ether. Examples of benzophenones are benzophenone, 2,4-dichlorobenzophenone, 4,4-dichlorobenzophenone, and p-chlorobenzophenone. One example of phosphine oxides is 2,4,6-trimethylbenzoyldiphenylphosphine oxide. Various examples of the compounds are described in the Newest UV Curing Technology (p. 159, issued by Kazuhiro Takatsu, published by Gijutsu Joho Kyokai, 1991), and these are useful in the invention. Preferred examples of commercially-available, photo-cleaving optical radical polymerization initiators are Ciba Speciality Chemicals' Irgacure (651, 184, 907). Preferably, the photopolymerization initiator is used in an amount of from 0.1 to 15 parts by weight relative to 100 parts by weight of the polyfunctional monomer, more preferably from 1 to 10 parts by weight. An optical sensitizer may be added to the photopolymerization initiator. Examples of the optical sensitizer are n-butylamine, triethylamine, tri-n-butyl phosphine, Michler's ketone, and thioxanthone.

[0030]

The thermal radical initiator includes organic or

inorganic peroxides, and organic azo and diazo compounds. Concretely, the organic peroxides include benzoyl peroxide, halogenobenzoyl peroxide, lauroyl peroxide, acetyl peroxide, dibutyl peroxide, cumene hydroperoxide, butyl hydroperoxide; the inorganic peroxides include hydrogen peroxide, ammonium persulfate, potassium persulfate; the azo compounds include 2-azobisisobutyronitrile, 2-azobispropionitrile, 2-azobiscyclohexane-dinitrile; and the diazo compounds include diazoaminobenzene, and p-nitrobenzene-diazonium.

[0031]

The polymer having a polyether backbone structure that is used as the binder for the low-refractive index layer is preferably a ring-opening polymer of a polyfunctional epoxy compound. The Ring-opening polymerization of a polyfunctional epoxy compound may be effected through exposure to active energy rays or to heat in the presence of an optical acid generator or a thermal acid generator. Accordingly, a coating liquid including a polyfunctional epoxy compound, an optical acid generator or a thermal acid generator, mat particles and an inorganic filler is prepared, and the coating liquid is applied onto a transparent support, and then polymerized and cured through exposure to active energy rays or to heat to form an antireflection film.

[0032]

In place of or in addition to the monomer that has two or more ethylenic unsaturated groups for obtaining a binder

polymer having a saturated hydrocarbon chain as the backbone structure and having a crosslinked structure, a monomer that has a crosslinking functional group may be used so as to introduce the crosslinking functional group into the polymer, and through the reaction of the crosslinking functional group, a crosslinked structure may be introduced into the binder polymer.

Examples of the crosslinking functional group are an isocyanate group, an epoxy group, an aziridine group, an oxazoline group, an aldehyde group, a carbonyl group, a hydrazine group, a carboxyl group, a methylol group, and an active methylene group. Vinylsulfonic acids, acid anhydrides, cyanoacrylate derivatives, melamines, etherified methylols, esters and urethanes, and metal alkoxides such as tetramethoxysilane may also be used as monomers for introducing a crosslinked structure into the polymer. A functional group that becomes crosslinkable as a result of decomposition reaction, such as a blocked isocyanate group may also be used. That is, in the invention, the crosslinking functional group may not be one that is directly reactive, but may be one that becomes reactive as a result of decomposition. The binder polymer having such a crosslinking functional group may be, after application onto a support, heated to form the intended crosslinked structure.

[0033]

Although not specifically limited, the surface free

energy lowering binder for use in the low-refractive index layer of the antireflection film of the invention may be any one that may significantly lower the surface free energy of the layer that is formed as a result of curing of an alkyl acrylate monomer such as typically DPHA, when the binder is added to the layer. Especially preferably, the binder is such that the surface free energy of the layer cured and formed only by the binder is at most 30 mN/m, more preferably at most 25 mN/m, even more preferably at most 20 mN/m. The binder is preferably a compound containing at least one group selected from a fluoroalkyl group, a dimethylsiloxane group, and a polydimethylsiloxane (so-called silicone) group. Before cured, the binder may be either monomer or polymer, or may be a mixture of monomer and polymer, or may be a mixture of multiple compounds.

[0034]

Preferred examples of the surface free energy lowering binder for use in the low-refractive index layer is described as below. The surface free energy lowering binder preferably includes a fluorine-containing polymer as a low-refractive index binder. The fluorine-containing polymer is preferably a fluorine-containing polymer that is crosslinked by heat or active energy rays with a kinematic friction factor of from 0.03 to 0.15 and a contact angle to water of from 90 to 120°.

[0035]

The fluorine-containing polymer for use in the low-

refractive index layer includes hydrolytic dewatering condensates of perfluoroalkyl group-containing silane compounds (e.g., (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane), as well as fluorine-containing copolymers that include, as the constitutive components thereof, fluorine-containing monomer units and structural units for imparting crosslinking reactivity to the polymer.

[0036]

Specific examples of the fluorine-containing monomer units are fluoro-olefins (e.g., fluoroethylene, vinylidene fluoride, tetrafluoroethylene, perfluoro-octylethylene, hexafluoropropylene, perfluoro-2,2-dimethyl-1,3-dioxol), partially or completely fluorinated alkyl ester derivatives of (meth)acrylic acid (e.g., Biscoat 6FM (by Osaka Yuki Kagaku), M-2020 (by Daikin)), and completely or partially fluorinated vinyl ethers. Preferred are perfluoro-olefins; and more preferred is hexafluoropropylene from the viewpoint of the refractive index, solubility, transparency and availability thereof.

[0037]

The structural units for imparting crosslinking reactivity to the polymer are, for example, structural units formed through polymerization of a monomer that intrinsically has a self-crosslinking functional group in the molecule, such as glycidyl (meth)acrylate or glycidyl vinyl ether;

structural units formed through polymerization of a monomer having a carboxyl group, a hydroxyl group, an amino group or a sulfo group (e.g., (meth)acrylic acid, methylol (meth)acrylate, hydroxyalkyl (meth)acrylate, allyl acrylate, hydroxyethyl vinyl ether, hydroxybutyl vinyl ether, maleic acid, crotonic acid); structural units constructed by introducing a crosslinking reactive group such as a (meth)acryloyl group into those structural units through polymerization reaction (for example, the group may be introduced according to a method of reacting acrylic acid chloride on a hydroxyl group).

[0038]

It may copolymerize monomers that do not appropriately have fluorine atoms other than the fluorine-containing monomer units and structural units for imparting crosslinking reactivity from the viewpoint of the solubility to a solvent, a transparency of the film, and the like. Although not specifically limited, combined usable monomers are, for example, olefins (e.g., ethylene, propylene, isoprene, vinyl chloride, vinylidene chloride), acrylic esters (e.g., methyl acrylate, methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate), methacrylic esters (e.g., methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethylene glycol methacrylate), styrene derivatives (e.g., styrene, divinylbenzen, vinyl toluene, α -methylstyrene), vinyl ethers (e.g., methyl vinyl ether, ethyl vinyl ether, cyclohexyl

vinyl ether), vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl cinnamate), acrylamides (e.g., N-tert-butylacrylamide, N-cyclohexylacrylamide), methacrylamides, acrylonitrile derivatives.

[0039]

Regarding the above-described polymer, a curing agent may also be used as the method disclosed in JP-A-H10-25388 and JP-A-H10-147739.

[0040]

The fluorine-containing polymer that is especially useful for the low-refractive index layer in the invention is a random copolymer of perfluoro-olefins with vinyl ethers or vinyl esters. Especially preferably, the polymer has a group that may be subjected to crosslinking reaction by itself (e.g., radical reactive group such as (meth)acryloyl group, and ring-opening polymerizing group such as epoxy group or oxetanyl group). Preferably, the content of the crosslinking reactive group-containing polymer units in the polymer is from 5 to 70 mol% of all the polymer units of the polymer, more preferably from 30 to 60 mol%.

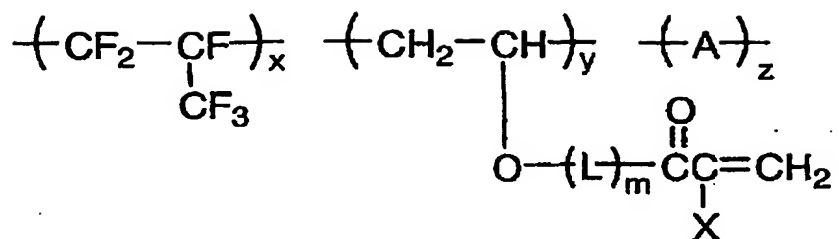
[0041]

One preferred embodiment of the copolymer (fluorine-containing polymer) for use in the low-refractive index layer is a polymer of the following formula 1:

[0042]

[CHEM. 2]

Formula 1



[0043]

In formula 1, L represents a linking group having from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 2 to 4 carbon atoms, and it may have a linear structure, or a branched structure, or a cyclic structure, and it may contain a hetero atom selected from O, N and S. Preferred examples of L are $^*-(\text{CH}_2)_2-\text{O}-^{**}$, $^*-(\text{CH}_2)_2-\text{NH}-^{**}$, $^*-(\text{CH}_2)_4-\text{O}-^{**}$, $^*-(\text{CH}_2)_6-\text{O}-^{**}$, $^*-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-^{**}$, $^*-\text{CONH}-(\text{CH}_2)_3-\text{O}-^{**}$, $^*-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{O}-^{**}$, $^*-\text{CH}_2\text{CH}_2\text{OCONH}(\text{CH}_2)_3-\text{O}-^{**}$ (in which * indicates the linking site on the backbone structure side; and ** indicates the linking side on the (meth)acryloyl group side). m indicates 0 or 1.

[0044]

In formula 1, X represents a hydrogen atom or a methyl group. From the viewpoint of the curing reactivity of the polymer, X is preferably a hydrogen atom.

[0045]

In formula 1, A represents a repetitive unit derived from a vinyl monomer, and, not specifically limited, it may be any constitutive component of a monomer copolymerizable with hexafluoropropylene. From the viewpoint of the

adhesiveness of the polymer to substrates, the T_g thereof (this contributes to the film hardness), the solubility thereof in solvent, the transparency thereof, the lubricity thereof, and the dust resistance and the stain resistance thereof, the unit A may be suitably selected. According to the object of the polymer, the repetitive unit A may be constituted by a repetitive unit derived from mono or a plurality of vinyl monomer.

[0046]

Preferred examples of the vinyl monomer are vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, t-butyl vinyl ether, cyclohexyl vinyl ether, isopropyl vinyl ether, hydroxyethyl vinyl ether, hydroxybutyl vinyl ether, glycidyl vinyl ether, allyl vinyl ether; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate; (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, hydroxyethyl (meth)acrylate, glycidyl methacrylate, allyl (meth)acrylate, (meth)acryloyloxypropyltrimethoxysilane; styrene derivatives such as styrene, p-hydroxymethylstyrene; unsaturated carboxylic acids and their derivatives such as crotonic acid, maleic acid, itaconic acid. More preferred are vinyl ether derivatives and vinyl ester derivatives; and even more preferred are vinyl ether derivatives.

[0047]

x, y and z each indicate the mol% of the constitutive components, and satisfy the following: $30 \leq x \leq 60$, $5 \leq y \leq 70$,

$0 \leq z \leq 65$. Preferably, $35 \leq x \leq 55$, $30 \leq y \leq 60$, $0 \leq z \leq 25$; more preferably $40 \leq x \leq 55$, $40 \leq y \leq 55$, $0 \leq z \leq 10$.

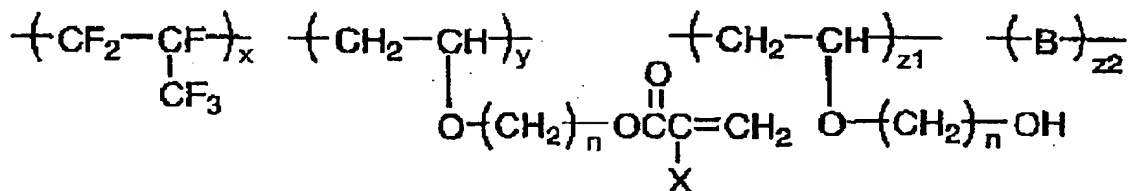
[0048]

A more preferred embodiment of the copolymer for use in the low-refractive index layer of the antireflection film of the invention is a polymer of the following formula 2:

[0049]

[CHEM. 3]

Formula 2

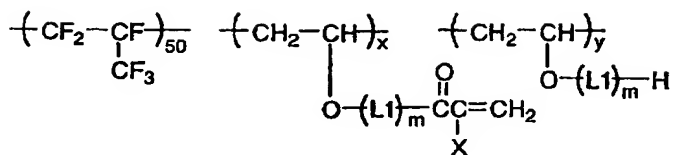


[0050]

In formula 2, X, x and y have the same meanings as those in formula 1, and their preferred ranges are the same as in formula 1. n indicates an integer of $2 \leq n \leq 10$, preferably $2 \leq n \leq 6$, more preferably $2 \leq n \leq 4$. B represents a repetitive unit derived from a vinyl monomer, and it may be composed of a single composition or multiple compositions. For its examples, referred to are those mentioned hereinabove for A in formula 1. z1 and z2 each indicate the mol% of the repetitive units, and satisfy $0 \leq z1 \leq 65$ and $0 \leq z2 \leq 65$. Preferably, $0 \leq z1 \leq 30$ and $0 \leq z2 \leq 10$; more preferably $0 \leq z1 \leq 10$ and $0 \leq z2 \leq 5$.

[0051]

[CHEM. 5]






				X		Number-Average Molecular Weight
	x	y	m	L1	X	M _n (×10 ⁴)
P-11	50	0	1	*-CH ₂ CH ₂ NH-	H	4.0
P-12	50	0	1	*-CH ₂ CH ₂ OCNHCH ₂ CH ₂ O- O	H	4.5
P-13	50	0	1	*-CH ₂ CH ₂ OCNHCH ₂ CH ₂ O- O	CH ₃	4.5
P-14	50	0	1	*-CH ₂ CH ₂ CH ₂ CH ₂ OCNHCH ₂ CH ₂ O- O	CH ₃	5.0
P-15	50	0	1	*-CH ₂ CH(OH)CH ₂ O-	H	3.5
P-16	50	0	1	*-CH ₂ CH(OH)CHO-	H	3.0
P-17	50	0	1	*-CH ₂ CH ₂ OCH ₂ -CH(OH)CH ₂ O-	H	3.0
P-18	50	0	1	*-CH ₂ OCH ₂ CH(OH)CH ₂ O-	CH ₃	3.0
P-19	50	0	1	*-CH ₂ OCH ₂ CH(OH)O-	CH ₃	3.0
P-20	40	10	1	*-CH ₂ CH ₂ O-	CH ₃	0.6

* indicates the side of the polymer backbone.

[0055]

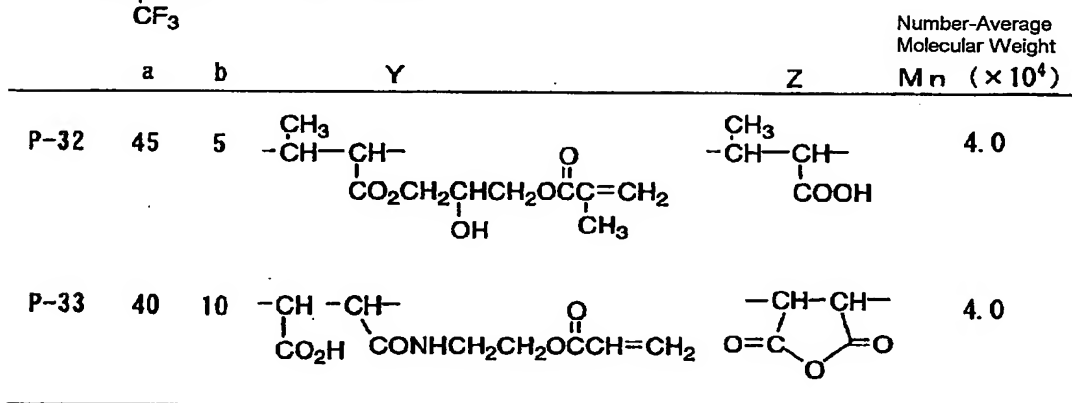
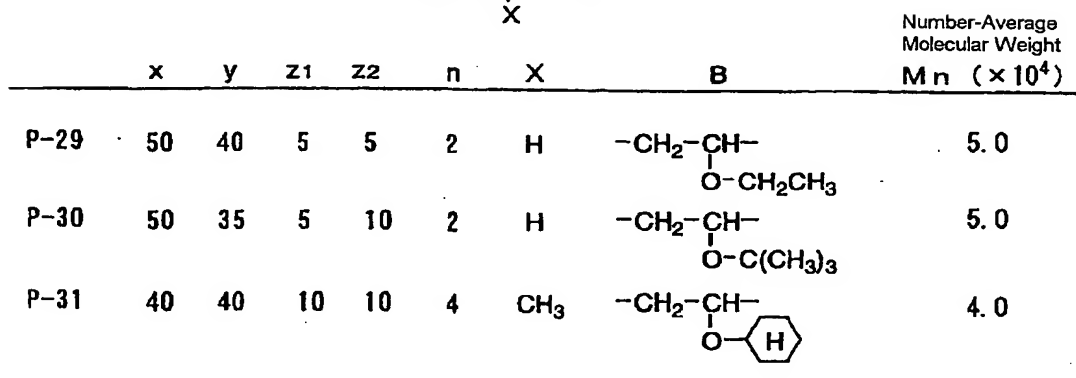
[CHEM. 6]

$\begin{array}{c} \text{-(CF}_2\text{-CF)}_a \\ \\ \text{CF}_3 \end{array} \quad \begin{array}{c} \text{-(CH}_2\text{-CH)}_b \\ \\ \text{O-L1-C(=O)-CH=CH}_2 \end{array} \quad \text{-(A)}_c$							Number-Average Molecular Weight $M_n (\times 10^4)$
	a	b	c	L1	A		
P-21	55	45	0	*-CH ₂ CH ₂ O-*	—		1.8
P-22	45	55	0	*-CH ₂ CH ₂ O-*	—		0.8
P-23	50	45	5	*-CH ₂ CH ₂ O-C(=O)-NH-CH ₂ CH ₂ O-*	-CH ₂ -CH- OCH ₂ CH ₂ OH		0.7
P-24	50	45	5	*-CH ₂ CH(OH)-CH ₂ O-*	-CH ₂ -CH- O-CH ₂ - 		4.0
P-25	50	45	5	*-CH ₂ CH(CH ₂ OH)-*	-CH ₂ -CH- O-CH ₂ - 		4.0
P-26	50	40	10	*-CH ₂ CH ₂ O-*	-CH ₂ -CH- OCH ₂ CH ₃		4.0
P-27	50	40	10	*-CH ₂ CH ₂ O-*	-CH ₂ -CH- O- 		4.0
P-28	50	40	10	*-CH ₂ CH ₂ O-*	-CH(CH ₃)-CH- COOH		5.0

* indicates the side of the polymer backbone. ** indicates the side of the acryloyl group.

[0056]

[CHEM. 7]



[CHEM. 8]

	$\begin{array}{c} \text{-(CH}_2\text{-CH)}_x \\ \\ \text{O=C} \\ \\ \text{O} \\ \\ \text{Rf} \end{array}$			$\begin{array}{c} \text{-(CH}_2\text{-CH)}_y \\ \\ \text{O=C} \\ \\ \text{O} \\ \\ \text{L-C(=O)CH=CH}_2 \end{array}$			$\begin{array}{c} \text{-(CH}_2\text{-CH)}_z \\ \\ \text{O=C} \\ \\ \text{O} \\ \\ \text{L-H} \end{array}$			Number-Average Molecular Weight M _n (×10 ⁴)
	x	y	z	Rf			L			
P-34	60	40	0	-CH ₂ CH ₂ C ₈ F ₁₇ -n			*-CH ₂ CH ₂ O-			11
P-35	60	30	10	-CH ₂ CH ₂ C ₄ F ₈ H-n			*-CH ₂ CH ₂ O-			30
P-36	40	60	0	-CH ₂ CH ₂ C ₆ F ₁₂ H			*-CH ₂ CH ₂ CH ₂ CH ₂ O-			4.0

* indicates the side of the polymer backbone.

	$\begin{array}{c} \text{-(CH}_2\text{-CH)}_x \\ \\ \text{O} \\ \\ \text{Rf} \end{array}$			$\begin{array}{c} \text{-(CH}_2\text{-CH)}_y \\ \\ \text{O} \\ \\ \text{O} \\ \\ \text{O} \end{array}$			$\begin{array}{c} \text{-(CH}_2\text{-CH)}_z \\ \\ \text{O} \end{array}$			Number-Average Molecular Weight M _n (×10 ⁴)
	x	y	z	n			Rf			
P-37	50	50	0	2			-CH ₂ C ₄ F ₈ H-n			5.0
P-38	40	55	5	2			-CH ₂ C ₄ F ₈ H-n			4.0
P-39	30	70	0	4			-CH ₂ C ₈ F ₁₇ -n			10
P-40	60	40	0	2			-CH ₂ CH ₂ C ₈ F ₁₆ H-n			5.0

[0058]

The copolymers for use in the invention can be produced by preparing a precursor such as a hydroxyl group-containing polymer according to various polymerization methods of, for example, solution polymerization, precipitation polymerization, suspension polymerization, precipitation polymerization, bulk polymerization or emulsion polymerization, and then introducing a (meth)acryloyl group

into it through the above-mentioned polymer reaction. The polymerization reaction may be effected in any known method of batch, or semi-continuous or continuous operation.

[0059]

To start the polymerization, employable is a method of using a radical initiator, or a method of exposing the system to light or radiation. The polymerization methods and the polymerization initiation methods are described, for example, in Teiji Tsuruta, *Methods of Polymer Synthesis*, revised edition (published by Nikkan Kogyo Shinbun, 1971); Takayuki Ohtsu & Masaetsu Kinoshita, *Experimental Methods of Polymer Synthesis* (published by Kagaku Dojin, 1972, pp. 124-154).

[0060]

Of the above-mentioned polymerization methods, especially preferred is a solution polymerization method that uses a radical initiator. The solvent usable in the solution polymerization method includes, for example, ethyl acetate, butyl acetate, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, tetrahydrofuran, dioxane, N,N-dimethylformamide, N,N-dimethylacetamide, benzene, toluene, acetonitrile, methylene chloride, chloroform, dichloroethane, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol. One or more such various organic solvents may be used either singly or in combination, or a mixed solvent thereof with water may also be used.

[0061]

The polymerization temperature must be set in relation to the molecular weight of the polymer to be produced and to the type of the initiator used. It may be from 0°C or lower to 100°C or higher, but is preferably from 50 to 100°C.

[0062]

The reaction pressure may be determined suitably, but generally falls between 1 and 100 kg/cm², preferably between 1 and 30 kg/cm². The reaction time may be between 5 and 30 hours or so.

[0063]

The reprecipitation solvent for the polymer obtained is preferably isopropanol, hexane, methanol or the like.

[0064]

A method of determining the segregation of a silicone or fluoroalkyl group on the surface of the low-refractive index layer is described. Using Shimadzu's ESCA-3400 (degree of vacuum, 1×10^{-5} Pa; X-ray source, target Mg; voltage, 12 kV; current, 20 mA), the photoelectric spectra, Si2P, F1s and Cls of the outermost surface of the antireflection film to be analyzed are measured; and the spectral intensity ratio Si2P/Cl s (=Si(a)) and F1s/Cl s (=F(a)) are calculated. Using the ion-etching unit (ion gun, voltage 2 kV, current 20 mA) of the device, ESCA-3400, the low-refractive index layer of the sample is cut off to have a height of 1/5 (± 5 %) of the original height thereof, and the photoelectric spectra, Si2P, F1s and Cls of the 80 % lower site of the layer are measured;

and the spectral intensity ratio Si2P/C1s ($=\text{Si(b)}$) and F1s/C1s ($=\text{F(b)}$) are calculated. The intensity change before and after the etching treatment, $\text{Si(a)}/\text{Si(b)}$, and $\text{F(a)}/\text{F(b)}$ are obtained. Accordingly, from the change of the Si2P/C1s ratio and the F1s/C1s ratio before and after the etching treatment (photoelectric spectral intensity ratio in the uppermost surface of the low-refractive index layer/photoelectric spectral intensity ratio in the 80 % lower layer from the uppermost surface of the low-refractive index layer), the surface segregation degree can be determined. F1s and C1s are the intensity read at the peak position of the photoelectric spectra. For Si2p, the intensity at the Si atom-derived peak position (with binding energy of 105 eV or so) of silicone (polydimethylsiloxane) is employed for the intensity ratio calculation, and this is differentiated from the Si atom derived from inorganic silica particles. Under various etching conditions, pre-experiments of gradually etching the surface of the low-refractive index layer in various samples are carried out, and based on the etching condition that reaches the underlying hard-coat layer or high-refractive index layer, the condition to reach a depth of 80 % is determined. When only the surface characteristics are controlled, the surface-segregating compound (i.e., the surface free energy lowering compound) described in the present specification may be suitably used, and only the necessary components may be selectively

positioned in the surface of the layer, and, as a result, the surface characteristics may be controlled independently of the inside characteristics of the film.

[0065]

A coating method of the antireflection film in the invention is described. Each layer of the antireflective film can be formed with dip coating method, air knife coating method, curtain coating method, roller coating method, die coating method, wire bar coating method, gravure coating method, or extrusion coating method. When each layer is coated with gravure coating method, a little coating solution as each layer of the antireflective film can be uniformly coated and preferred. Micro-gravure coating method in the gravure coating method has a high film thickness uniformity and is more preferred. Through using the die coating method, a small amount of coating solution also can be coated with a high film thickness uniformity. The die coating method can easily control the film thickness since the die coating method is a pre-weighing method and is particularly preferred since evaporation of the solvent in the coating site is low. Two or more layers may be coated simultaneously. Simultaneous coating is disclosed in U.S. Patents 2761791, 2941898, 3508947, 3526528, and Yuji Harasaki, Coating Kogaku, p. 253, Asakura Shoten (1973).

[0066]

The hydrolysate and/or its partial condensate of the

organosilane compound for use in the invention, or that is, the sol component (the same shall apply hereinafter) is described in detail hereinafter.

The organosilane compound is represented by the following formula (A):



In formula (A), R^{10} represents a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group. The alkyl group includes methyl, ethyl, propyl, isopropyl, hexyl, t-butyl, sec-butyl, hexyl, decyl, hexadecyl. The alkyl group preferably has from 1 to 30 carbon atoms, more preferably from 1 to 16 carbon atoms, even more preferably 1 to 6 carbon atoms. The aryl group includes phenyl, naphthyl, and is preferably a phenyl group.

[0067]

X represents a hydroxyl group or a hydrolyzable group. The hydrolyzable group includes, for example, an alkoxy group (preferably having from 1 to 5 carbon atoms, e.g., methoxy, ethoxy), a halogen atom (e.g., Cl, Br, I), and $R^2\text{COO}$ (where R^2 is preferably a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms; its examples are CH_3COO , $\text{C}_2\text{H}_5\text{COO}$). Preferably, it is an alkoxy group, more preferably a methoxy group or an ethoxy group. m indicates an integer of from 1 to 3. Multiple R^{10} 's or X's, if any, in the compound may be the same or different. m is preferably 1 or 2, more preferably 1.

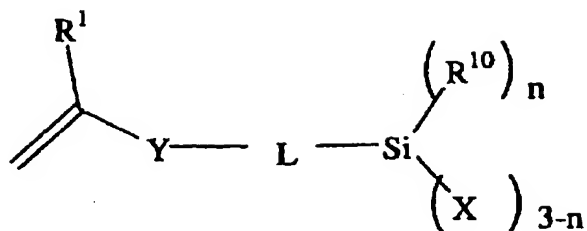
[0068]

Although not specifically limited, the substituent that may be in R^{10} includes, for example, a halogen atom (e.g., fluorine atom, chlorine atom, bromine atom), a hydroxyl group, a mercapto group, a carboxyl group, an epoxy group, an alkyl group (e.g., methyl, ethyl, i-propyl, propyl, t-butyl), an aryl group (e.g., phenyl, naphthyl), an aromatic heterocyclic group (e.g., furyl, pyrazolyl, pyridyl), an alkoxy group (e.g., methoxy, ethoxy, i-propoxy, hexyloxy), an aryloxy group (e.g., phenoxy), an alkylthio group (e.g., methylthio, ethylthio), an arylthio group (e.g., phenylthio), an alkenyl group (e.g., vinyl, 1-propenyl), an acyloxy group (e.g., acetoxy, acryloyloxy, methacryloyloxy), an alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), a carbamoyl group (e.g., carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-methyl-N-octylcarbamoyl), an acylamino group (e.g., acetylamino, benzoylamino, acrylamino, methacrylamino). These substituents may be further substituted. Of multiple R^{10} 's, if any, in the compound, at least one is preferably a substituted alkyl group or a substituted aryl group. In particular, vinyl-polymerizing substituent-having organosilane compounds of a formula (B) are preferred for use herein.

[0069]

Formula (B)

[CHEM. 9]



[0070]

In formula (B), R^1 represents a hydrogen atom, or a methyl group, a methoxy group, an alkoxycarbonyl group, a cyano group, a fluorine atom, or a chlorine atom. The alkoxycarbonyl group includes methoxycarbonyl and ethoxycarbonyl. Preferably, R^1 is a hydrogen atom, a methyl group, a methoxy group, a methoxycarbonyl group, a cyano group, a fluorine atom or a chlorine atom, more preferably a hydrogen atom, a methyl group, a methoxycarbonyl group, a fluorine atom or a chlorine atom, even more preferably a hydrogen atom or a methyl group. Y represents a single bond or an ester group, an amido group, an ether group or a urea group. Preferably, Y is a single bond, an ester group or an amido group, more preferably a single bond or an ester group, even more preferably an ester group.

[0071]

L represents a divalent linking chain. Concretely, it represents a substituted or unsubstituted alkylene group, a substituted or unsubstituted arylene group, a substituted or unsubstituted alkylene group having a linking group (e.g., ether, ester, amido) inside it, or a substituted or

unsubstituted arylene group having a linking group inside it; preferably, it is substituted or unsubstituted alkylene group having from 2 to 10 carbon atoms, a substituted or unsubstituted arylene group having from 6 to 20 carbon atoms, or an alkylene group having from 3 to 10 carbon atoms and having a linking group inside it; more preferably an unsubstituted alkylene group, an unsubstituted arylene group, or an alkylene group having an ether or ester linking group inside it; even more preferably an unsubstituted alkylene group, or an alkylene group having an ether or ester linking group inside it. The substituent for these includes a halogen atom, a hydroxyl group, a mercapto group, a carboxyl group, an epoxy group, an alkyl group and an aryl group, and these substituents may be further substituted.

[0072]

n indicates 0 or 1. Multiple X's, if any, in the compound may be the same or different. n is preferably 0. R¹⁰ has the same meaning as in formula (A), and is preferably a substituted or unsubstituted alkyl group, or an unsubstituted aryl group, more preferably an unsubstituted alkyl group or an unsubstituted aryl group. X has the same meaning as in formula (A), and is preferably a halogen atom, a hydroxyl group, or an unsubstituted alkoxy group, more preferably a chlorine atom, a hydroxyl group or an alkoxy group having from 1 to 6 carbon atoms, even more preferably a hydroxyl group or an alkoxy group having from 1 to 3 carbon

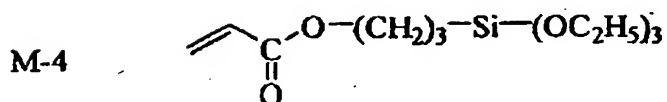
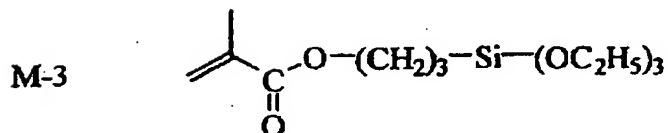
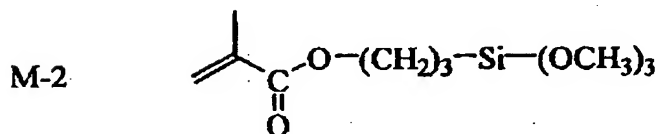
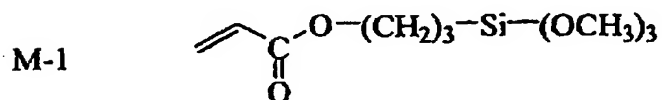
atoms, still more preferably a methoxy group.

[0073]

Two or more different types of the compounds of formula (A) and formula (B) may be used herein, as combined. Specific examples of the compounds of formula (A) and formula (B) are shown below, to which, however, the invention is not limited.

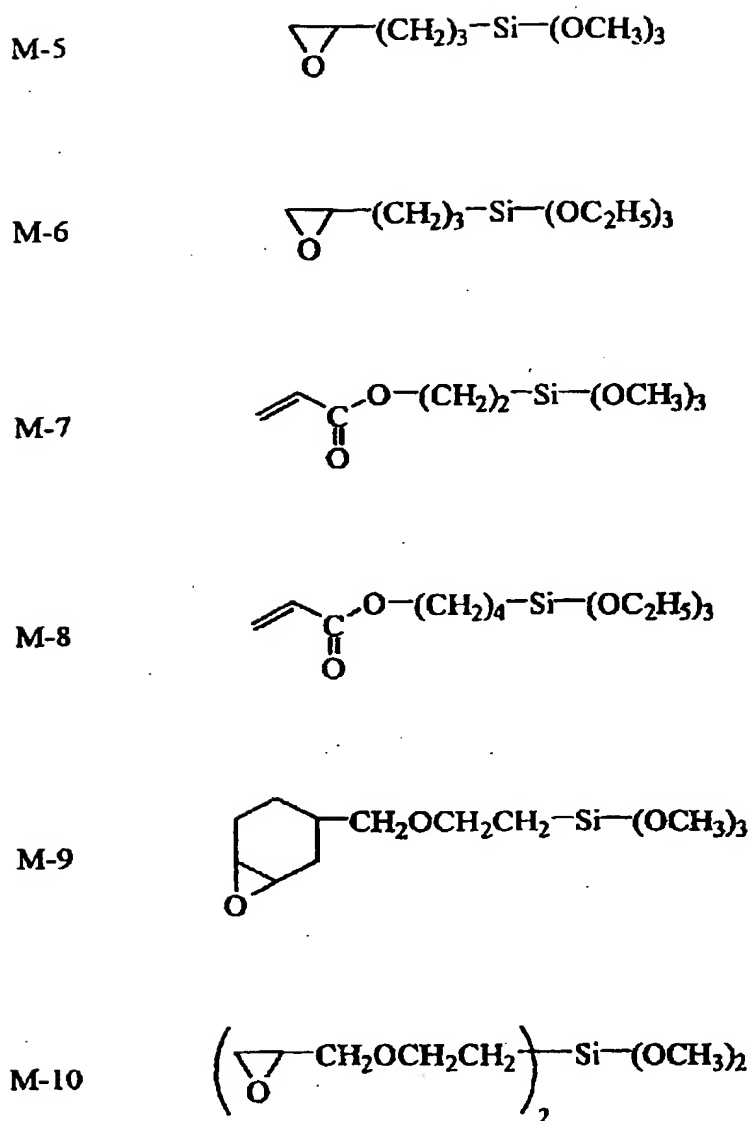
[0074]

[CHEM. 10]



[0075]

[CHEM. 11]



[0076]

Of these examples, (M-1), (M-2) and (M-5) especially are preferred.

[0077]

(Acid Catalyst, Metal Chelate Compound)

It is desirable that the hydrolysates and/or

condensates (sol component) of organosilanes are prepared in the presence of a catalyst. The catalyst includes inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid; organic acids such as oxalic acid, acetic acid, formic acid, methanesulfonic acid, toluenesulfonic acid; inorganic bases such as sodium hydroxide, potassium hydroxide, ammonia; organic bases such as triethylamine, pyridine; and metal alkoxides such as aluminium triisopropoxide, zirconium tetrabutoxide. In view of the production stability and storage stability of the liquid of inorganic oxide fine particles, acid catalysts (inorganic acids, organic acids) and/or metal chelate compounds are used in the invention. The inorganic acid is preferably hydrochloric acid or sulfuric acid; and the organic acid preferably has an acid dissociation constant in water (pK_a value at 25°C) of at most 4.5. More preferred are hydrochloric acid, sulfuric acid, and organic acids having an acid dissociation constant in water of at most 3.0; even more preferred are hydrochloric acid, sulfuric acid, and organic acids having an acid dissociation constant in water of at most 2.5; still more preferred are organic acids having an acid dissociation constant in water of at most 2.5; further more preferred are methanesulfonic acid, oxalic acid, phthalic acid, and malonic acid; especially preferred is oxalic acid.

[0078]

When the hydrolyzable group of the organosilane is an

alkoxy group and the acid catalyst is an organic acid, then the carboxyl group or the sulfo group of the organic acid may supply protons, and therefore the amount of water to be added may be reduced. Concretely, the amount of water to be added to the reaction system may be from 0 to 2 mols, preferably from 0 to 1.5 mols, more preferably from 0 to 1 mol, even more preferably 0 to 0.5 mols, relative to 1 mol of the alkoxide group of the organosilane. When an alcohol is used as the solvent, then an embodiment of adding substantially no water to the system is also preferred.

[0079]

The amount of the acid catalyst to be used is described. When the acid catalyst is an inorganic acid, then its amount may be from 0.01 to 10 mols, preferably from 0.1 to 5 mols relative to the hydrolysable group; but when the acid catalyst is an organic acid, then the most preferred amount varies depending on the amount of water added to the system. Concretely, when water is added to the system, the amount of the organic acid to be added thereto may be from 0.01 to 10 mol%, preferably from 0.1 to 5 mol% relative to the hydrolysable group. However, when substantially no water is added, then the amount of the organic acid to be added may be from 1 to 500 mol%, preferably from 10 to 200 mol%, even more preferably from 20 to 200 mol%, still more preferably from 50 to 150 mol%, further more preferably from 50 to 120 mol% relative to the hydrolysable group.

The treatment may be attained by stirring the system at 15 to 100°C, and it suitably controlled depending on the reactivity of the organosilane.

[0080]

Although not specifically limited, any metal chelate compound having a center metal selected from Zr, Ti or Al may be preferably used herein. Within the category, two or more different types of metal chelate compounds may be used as combined. Specific examples of the metal chelate compound for use in the invention are zirconium chelate compounds such as tri-n-butoxyethylacetacetate zirconium, di-n-butoxybis(ethylacetacetate) zirconium, n-butoxytris(ethylacetacetate) zirconium, tetrakis(n-propylacetacetate) zirconium, tetrakis(acetylacetacetate) zirconium, tetrakis(ethylacetacetate) zirconium; titanium chelate compounds such as diisopropoxy-bis(ethylacetacetate) titanium, diisopropoxy-bis(acetylacetate) titanium, diisopropoxy-bis(acetylacetone) titanium; aluminium chelate compounds such as diisopropoxyethylacetacetate aluminium, diisopropoxyacetylacetnate aluminium, isopropoxybis(ethylacetacetate) aluminium, isopropoxybis(acetylacetionate) aluminium, tris(ethylacetacetate) aluminium, tris(acetylacetionate) aluminium, monoacetylacetionate-bis(ethylacetacetate) aluminium.

Of those metal chelate compounds, preferred are tri-n-

index layer is at most 3 %.

[0083]

For the high-refractive index layer and the middle-refractive index layer in the invention, preferably used is a cured product of a composition that is prepared by dispersing inorganic fine particles having a high refractive index in a monomer, an initiator and an organic substituted silicon compound such as those described hereinabove for the hard-coat layer. The inorganic fine particles are preferably oxides of metal (e.g., aluminium, titanium, zirconium, antimony). In view of their refractive index, most preferred are fine particles of titanium dioxide. When a monomer and an initiator are used, then the coating layer is cured through exposure to active energy rays or heat for polymerization, whereby it gives a middle-refractive index layer or a high-refractive index layer having good scratch-resistance and good adhesiveness. Preferably, the mean particle size of the inorganic fine particles is from 10 to 100 nm.

[0084]

The fine particles of titanium dioxide are especially preferably inorganic fine particles including titanium dioxide as the principal ingredient thereof and containing at least one element selected from cobalt, aluminum and zirconium. The principal ingredient as referred to herein means that its content (% by weight) is the largest of all

the constitutive ingredients of the particles. In the invention, the inorganic fine particles that include titanium dioxide as the principal ingredient thereof preferably have a refractive index of from 1.90 to 2.80, more preferably from 2.10 to 2.80, even more preferably from 2.20 to 2.80. Also preferably, the weight-average particle size of the primary particles of the inorganic fine particles that include titanium dioxide as the principal ingredient thereof is from 1 to 200 nm, more preferably from 1 to 150 nm, even more preferably from 1 to 100 nm, still more preferably from 1 to 80 nm.

[0085]

The particle size of the inorganic fine particles may be determined according to a light scattering method or through electro microscopy. Preferably, the specific surface area of the inorganic fine particles is from 10 to 400 m²/g, more preferably from 20 to 200 m²/g, most preferably from 30 to 150 m²/g. Also preferably, the crystal structure of the inorganic fine particles that include titanium dioxide as the principal ingredient thereof includes a rutile structure, a mixed rutile/anatase structure, an anatase structure or an amorphous structure as the principal ingredient thereof. More preferably, it includes a rutile structure as the principal ingredient thereof. The principal ingredient as referred to herein means that its content (% by weight) is the largest of all the constitutive ingredients of the

particles.

[0086]

Containing at least one element selected from Co (cobalt), Al (aluminium) and Zr (zirconium), the inorganic fine particles that include titanium dioxide as the principal ingredient thereof may retard the photocatalytic activity of titanium dioxide therein and are therefore effective for improving the weather resistance of the high-refractive index layer and the middle-refractive index layer in the invention. Especially preferably, the additional element is Co (cobalt). Also preferably, two or more different types of additional elements may be in the inorganic fine particles.

[0087]

<Dispersant>

A dispersant may be used for dispersing the inorganic fine particles that include titanium dioxide as the principal ingredient thereof, in the high-refractive index layer and the middle-refractive index layer in the invention. Preferably, an anionic group-having dispersant is used for dispersing the inorganic fine particles that include titanium dioxide as the principal ingredient thereof. For the anionic group, effectively used are an acidic proton-having group such as a carboxyl group, a sulfonic acid group (and a sulfo group), a phosphoric acid group (and a phosphono group), a sulfonamido group, and their salts. More preferred are a carboxyl group, a sulfonic acid group, a phosphoric acid

group and their salts; and even more preferred are a carboxyl group and a phosphoric acid group. The number of the anionic groups to be in one molecule of the dispersant may be at least one. For further improving the dispersibility of the inorganic fine particles, multiple anionic groups may be in the dispersant. Preferably, at least two anionic groups may be in the dispersant on average, more preferably at least 5 anionic groups, even more preferably at least 10 anionic groups therein. One molecule of the dispersant may contain different types of anionic groups.

[0088]

Also preferably, the dispersant contains a crosslinking or polymerizing functional group. The crosslinking or polymerizing functional group includes an ethylenic unsaturated group that may undergo radical addition reaction or polymerization (e.g., (meth)acryloyl, allyl, styryl, vinyloxy), a cationic polymerizing group (e.g., epoxy, oxetanyl, vinyloxy), a polycondensation-reactive group (e.g., hydrolyzing silyl, N-methylol). Preferred is an ethylenic unsaturated group-having functional group. The dispersant to be used for dispersing the inorganic fine particles that include titanium dioxide as the principal ingredient thereof in the high-refractive index layer in the invention preferably has an anionic group and a crosslinking or polymerizing functional group, in which the crosslinking or polymerizing functional group is preferably in the side

branches of the dispersant. Although not specifically limited, the weight-average molecular weight (Mw) of the dispersant that has an anionic group and a crosslinking or polymerizing functional group, in which the crosslinking or polymerizing functional group is in the side branches of the dispersant, is preferably at least 1,000. More preferably, the weight-average molecular weight (Mw) of the dispersant is from 2,000 to 1,000,000, even more preferably from 5,000 to 200,000, still more preferably from 10,000 to 100,000.

[0089]

The amount of the dispersant to be used is preferably from 1 to 50 % by weight of the inorganic fine particles, more preferably from 5 to 30 % by weight, most preferably from 5 to 20 % by weight. Two or more different types of the dispersants may be used herein, as combined.

[0090]

<Method of Forming High (Middle)-Refractive Index Layer>

The inorganic fine particles that include titanium dioxide as the principal ingredient thereof is used as the dispersion thereof in forming the high-refractive index layer and the middle-refractive index layer in the invention. The inorganic fine particles are dispersed in a dispersion medium in the presence of the above-mentioned dispersant. The dispersion medium is preferably a liquid having a boiling point of from 60 to 170°C. Examples of the dispersion medium

are water, alcohols (e.g., methanol, ethanol, isopropanol, butanol, benzyl alcohol), ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone), esters (e.g., methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methyl formate, ethyl formate, propyl formate, butyl formate), aliphatic hydrocarbons (e.g., hexane, cyclohexane), halogenohydrocarbons (e.g., methylene chloride, chloroform, carbon tetrachloride), aromatic hydrocarbons (e.g., benzene, toluene, xylene), amides (e.g., dimethylformamide, dimethylacetamide, n-methylpyrrolidone), ethers (e.g., diethyl ether, dioxane, tetrahydrofuran), ether alcohols (e.g., 1-methoxy-2-propanol). Preferred for the dispersion medium are toluene, xylene, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and butanol; and more preferred are methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone.

[0091]

The inorganic fine particles are dispersed with a disperser. Examples of the disperser are sand grinder mill (e.g., bead mill with pin), high-speed impeller mill, pebble mill, roller mill, attritor and colloid mill. Especially preferred are sand grinder mill and high-speed impeller mill. The particles may be subjected to pre-dispersion treatment. Examples of the disperser to be used for pre-dispersion treatment are ball mill, three-roll mill, kneader and extruder. Preferably, the inorganic fine particles are

dispersed as fine as possible in the dispersion medium, and the weight-average particle size of the particles dispersed therein is from 1 to 200 nm, preferably from 5 to 150 nm, more preferably from 10 to 100 nm, even more preferably from 10 to 80 nm. Finely dispersed to at most 200 nm in size, the inorganic fine particles may be in the high-refractive index layer and the middle-refractive index layer not detracting from the transparency of the layers.

[0092]

Preferably, the high-refractive index layer and the middle-refractive index layer in the invention are formed as follows: To the dispersion prepared by dispersing the inorganic fine particles in the dispersion medium as in the above, preferably added are a binder precursor necessary for matrix formation (e.g., active energy ray-curable polyfunctional monomer or polyfunctional oligomer that will be mentioned hereinbelow), and a photopolymerization initiator to prepare a coating composition for high-refractive index layer and middle-refractive index layer, and the coating composition is applied onto a transparent support and this is then cured thereon through crosslinking reaction or polymerization of the active energy ray-curable compound (e.g., polyfunctional monomer or polyfunctional oligomer) to form the intended high-refractive index layer or middle-refractive index layer.

[0093]

Preferably, simultaneously with or after the coating operation to form the high-refractive index layer and the middle-refractive index layer, the binder for the layer is crosslinked or polymerized with the dispersant. The binder in the high-refractive index layer and the middle-refractive index layer thus formed takes the anionic group of the dispersant therein, for example, through the crosslinking or polymerization reaction of the above-mentioned preferred dispersant and the active energy ray-curable polyfunctional monomer or polyfunctional oligomer. In addition, the anionic group in the binder in the high-refractive index layer and the low-refractive index layer has the function of keeping the dispersion condition of the inorganic fine particles, and the crosslinked or polymerized structure thereof makes the binder have a film-forming ability, and after all, the binder improves the physical strength, the chemical resistance and the weather resistance of the inorganic fine particles-containing high-refractive index layer and middle-refractive index layer.

[0094]

The functional group of the active energy ray-curable polyfunctional monomer or polyfunctional oligomer is preferably one that is polymerizable through exposure to light, electron rays or radiations. Above all, it is more preferably a photopolymerizing functional group. The photopolymerizing functional group is, for example, an

unsaturated polymerizing functional group such as a (meth)acryloyl group, a vinyl group, a styryl group and an allyl group. Above all, preferred is a (meth)acryloyl group. In this description, the expressions of "(meth)acrylate" and "(meth)acryloyl" mean "acrylate or methacrylate", and "acryloyl or methacryloyl", respectively.

[0095]

Specific examples of the photopolymerizing functional group-having photopolymerizing polyfunctional monomer are alkylene glycol (meth)acrylic diesters such as neopentyl glycol acrylate, 1,6-hexanediol di(meth)acrylate, propylene glycol di(meth)acrylate; polyoxyalkylene glycol (meth)acrylic diesters such as triethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate;

[0096]

Polyalcohol (meth)acrylic diesters such as pentaerythritol di(meth)acrylate; ethylene oxide or propylene oxide adduct (meth)acrylic diesters such as 2,2-bis{4-(acryloxy-diethoxy)phenyl}propane, 2,2-bis{4-acryloxy-polypropoxy}phenyl}propane, and the like.

[0097]

Further, epoxy (meth)acrylates, urethane (meth)acrylates and polyester (meth)acrylates are also preferred for the photopolymerizing polyfunctional monomer.

[0098]

Above all, preferred are esters of polyalcohols and (meth)acrylic acid. More preferred are polyfunctional monomers having at least 3 (meth)acryloyl groups in one molecule. Concretely, they are trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, 1,2,4-cyclohexane tetra(meth)acrylate, glycerol triacrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol triacrylate, dipentaerythritol pentaacrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, tripentaerythritol triacrylate, and tripentaerythritol hexaacrylate.

[0099]

Two or more different types of polyfunctional monomers may be used herein as combined. Preferably, a photopolymerization initiator is used for the polymerization of the photopolymerizing polyfunctional monomer. The photopolymerization initiator is preferably a photo-radical polymerization initiator and a photo-cationic polymerization initiator. More preferred is a photo-radical polymerization initiator. The photo-radical polymerization initiator includes, for example, acetophenones, benzophenones, Michler's benzoylbenzoate, α -amylloxime esters, tetramethylthiuram monosulfide and thioxanthenes.

[0100]

Some photo-radical polymerization initiators are

commercially available, and, for example, they are Nippon Kayaku's KAYACURE (DETX-S, BP-100, BDMK, CTX, BMS, 2-EAQ, ABQ, CPTX, EPD, ITX, QTX, BTC, MCA), Ciba-Speciality Chemicals' Irgacure (651, 184, 500, 907, 369, 1173, 2959, 4265, 4263), Sartomer's Esacure (KIP100F, KB1, EB3, BP, X33, KT046, KT37, KIP150, TZT).

[0101]

In particular, a photo-cleavable photo-radical polymerization initiator is preferred for use herein. The photo-cleavable photo-radical polymerization initiator is described, for example, in The Latest UV Curing Technology (p. 159, issued by Kazuhiro Takahashi, published by the Technology Information Association, 1991). Some photo-curable photo-radical polymerization initiators are commercially available, and for example, they are Ciba-Speciality Chemicals' Irgacure (651, 184, 907).

[0102]

Preferably, the photopolymerization initiator is used in an amount of from 0.1 to 15 parts by weight relative to 100 parts by weight of the polyfunctional monomer, more preferably from 1 to 10 parts by weight. A photosensitizer may be used in addition to the photopolymerization initiator. Specific examples of the photosensitizer are n-butylamine, triethylamine, tri-n-butyl phosphine, Michler's ketone and thioxanthone. Some photosensitizers are commercially available, and, for example, they are Nippon Kayaku's

KAYACURE (DMBI, EPA). Preferably, the photopolymerization reaction is attained through exposure to UV rays after coating and drying of the high-refractive index layer. The high-refractive index layer in the invention may contain a compound of formula (A) mentioned above and/or its derivative compound.

[0103]

For forming a low-refractive index layer on the high-refractive index layer to construct the antireflection film, the refractive index of the high-refractive index layer is preferably from 1.55 to 2.40, more preferably from 1.60 to 2.20, even more preferably from 1.65 to 2.10, most preferably from 1.80 to 2.00.

[0104]

The high-refractive index layer may contain resin, surfactant, antistatic agent, coupling agent, viscosity improver, coloration inhibitor, colorant (pigment, dye), defoaming agent, leveling agent, flame retardant, UV absorbent, IR absorbent, tackifier, polymerization inhibitor, antioxidant, surface modifier, conductive metal fine particles, in addition to the above-mentioned components (inorganic fine particles, polymerization initiator, photosensitizer).

[0105]

In forming the high-refractive index layer, it is desirable that the crosslinking reaction or the

polymerization reaction of the active energy ray-curable compound is attained in an atmosphere having an oxygen concentration of at most 10 % by volume. Formed in the atmosphere having an oxygen concentration of at most 10 % by volume, the advantages of the high-refractive index layer are that its physical strength, chemical resistance and weather resistance are improved and, in addition, its adhesiveness to the high-refractive index layer and its adjacent layer is improved. Preferably, the crosslinking reaction or the polymerization reaction of the active energy ray-curable compound to form the layer is effected in an atmosphere having an oxygen concentration of at most 6 % by volume, more preferably at most 4 % by volume, even more preferably at most 2 % by volume, most preferably at most 1 % by volume.

[0106]

When the antireflection film is applied to liquid crystal display devices, an undercoat layer with particles having a mean particle size of from 0.1 to 10 μm added thereto may be additionally formed or the particles may be added to the hard-coat layer to give a light-scattering hard-coat layer, for the purpose of further improving the viewing angle characteristics of the film. The mean particle size of the particles is preferably from 0.2 to 5.0 μm , more preferably from 0.3 to 4.0 μm , even more preferably from 0.5 to 3.5 μm .

[0107]

The refractive index of the particles is preferably from 1.35 to 1.80, more preferably from 1.40 to 1.75, even more preferably from 1.45 to 1.75. The particle size distribution of the particles is preferably as narrow as possible. The particle size distribution of the particles may be indicated by an S value represented by the following formula, and it is preferably at most 1.5, more preferably at most 1.0, even more preferably at most 0.7.

$$S = [D(0.9) - D(0.1)] / D(0.5)$$

wherein

D(0.1) means a 10 %-corresponding particle size of the integral value of the volume-equivalent particle size;

D(0.5) means a 50 %-corresponding particle size of the integral value of the volume-equivalent particle size;

D(0.9) means a 90 %-corresponding particle size of the integral value of the volume-equivalent particle size.

[0108]

Preferably, the difference between the refractive index of the particles and the refractive index of the undercoat layer is at least 0.02, more preferably from 0.03 to 0.5, even more preferably from 0.05 to 0.4, still more preferably from 0.07 to 0.3. The particles to be added to the undercoat layer may be the inorganic particles or the organic particles described hereinabove for the antiglare layer. Preferably, the undercoat layer is formed between the hard-coat layer and the transparent support. As the case may be, the undercoat

layer may serve also as a hard-coat layer. When the particles having a mean particle size of from 0.1 to 10 μm are added to the undercoat layer, then the haze of the undercoat layer is preferably from 3 to 60 %, more preferably from 5 to 50 %, even more preferably from 7 to 45 %, still more preferably from 10 to 40 %.

[0109]

It is preferred to use plastic films as the transparent support of the reflection-preventing film of the invention. The examples of the polymers to form plastic films include cellulose ester (e.g., triacetyl cellulose, diacetyl cellulose), polyamide, polycarbonate, polyester (e.g., polyethylene terephthalate, polyethylene naphthalate), polystyrene, polyolefin, norbornene resin (e.g., Arton, trade name, manufactured by JSR Corporation), and amorphous polyolefin (Zeonex, trade name, manufactured by Zeon Corporation). Of these polymers, triacetyl cellulose, polyethylene terephthalate and polyethylene naphthalate are preferred, and triacetyl cellulose is particularly preferred. When the antireflective film of the invention is used for a liquid crystal display, the film is arranged at the outermost surface of the display by a means of providing an adhesive layer on one side of the film and the like. In the case where triacetyl cellulose is used as the transparent support, since triacetyl cellulose is used as the protective film for protecting the polarizing sheet of the polarizing plate, it

is preferred to use the reflection-preventing film of the invention as the protective film as it is in view of the cost.

[0110]

<Transparent support>

It is preferred for a reflection-preventing film to have a transparent substrate (a transparent support) exclusive of the case where a reflection-preventing film is directly provided on a CRT image display surface and the surface of a lens. The light transmittance of a transparent substrate is preferably 80 % or more, more preferably 86 % or more. The haze value of a transparent substrate is preferably 2.0 % or less, more preferably 1.0 % or less. The refractive index of a transparent substrate is preferably from 1.4 to 1.7. As a transparent substrate, plastic films are preferred to a glass plate. The examples of the materials of plastic films include cellulose ester, polyamide, polycarbonate, polyester (e.g., polyethylene terephthalate, polyethylene naphthalate, poly-1,4-cyclohexanedimethylene terephthalate, polyethylene-1,2-diphenoxyethane-4,4'-dicarboxylate, polybutylene terephthalate), polystyrene (e.g., syndiotactic polystyrene), polyolefin (e.g., polypropylene, polyethylene, polymethylpentene), polysulfone, polyether sulfone, polyallylate, polyether imide, polymethyl methacrylate and polyether ketone. Of these, cellulose ester, polycarbonate, polyethylene terephthalate and polyethylene naphthalate are preferred. In particular, when a transparent

substrate is used in a liquid crystal display, cellulose acylate film is preferably used. Cellulose acylate is manufactured from cellulose by esterification. Not that the above particularly preferred celluloses are used as they are, but linters, kenafs and pulps are refined and used.

[0111]

In the invention, cellulose acylate means carboxylic ester, preferably lower carboxylic ester, more preferably carboxylic ester film of cellulose. The carboxylic ester means carboxylic ester having 6 or fewer carbon atoms. Cellulose acylate having 2 to 4 carbon atoms is preferred. Cellulose acetate is particularly preferred. Mixed carboxylic esters such as cellulose acetate propionate or cellulose acetate butyrate are preferably used.

[0112]

The viscosity average degree of polymerization (DP) of cellulose acylate is preferably 250 or more, more preferably 290 or more. Preferably, the molecular weight distribution of Mw/Mn measured by gel permeation chromatography is narrow. The ratio of Mw/Mn (Mw and Mn are an weight-average molecular weight and an number-average molecular weight, respectively) is preferably from 1.0 to 5.0, more preferably from 1.0 to 3.0, even more preferably from 1.0 to 2.0. As the transparent support in the invention, preferably, cellulose acetate having acetification of 55.0 to 62.5 % is used, more preferably 57.0 to 62.0 %, even more preferably 59.0 to

61.5 %. The acetification means bond amount of acetic acid per cellulose unit weight. The acetification can be determined by measurement and calculation of acylation in ASTM: D-817-91 (testing methodology for cellulose acylates or the like).

[0113]

In the cellulose acylate, 2nd, 3rd, and 6th hydroxyls of cellulose may not be uniformly substituted, but substitution degree of 6th hydroxyl tends to decrease. In the cellulose acylate used in the invention, the substitution degree of 6th hydroxyl is preferably the same or greater than of 2nd and 3rd hydroxyl. The ratio of the substitution degree of 6th hydroxyl is preferably 30 to 40 % to the sum of the substitution degree of 2nd, 3rd, and 6th hydroxyls, more preferably 31 to 40 %, and most preferably 32 to 40%. A cellulose acylate film practically not containing a halogenated hydrocarbon, such as dichloromethane, and its preparation method are described in Hatsumei Kyokai Kokai Giho (Kogi No. 2001-1745, March 15, 2001; hereinafter Kokai Giho 2001-1745), and the cellulose acylate described therein are preferably used in the invention.

[0114]

Various additives can be added to the transparent support for the purpose of adjusting the mechanical characteristics (e.g., film strength, curling, dimensional stability, sliding property) and durability (e.g., humidity

and thermal resistance, weatherproofness) of the film. For example, plasticizers (e.g., phosphoric esters, phthalic esters, esters of oilyol and fatty acid), ultraviolet inhibitors (e.g., hydroxybenzophenone compounds, benzotriazole compounds, salicylic ester compounds, cyanoacrylate compounds), deterioration preventives (e.g., antioxidants, peroxide decomposer, radical inhibitors, metal deactivator, acid capturers, amine), fine particles (e.g., SiO_2 , Al_2O_3 , TiO_2 , BaSO_4 , CaCO_3 , MgCO_3 , talc, kaolin), removers, antistatic agents and infrared absorbers can be exemplified. These are described in detail in Hatsumei Kyokai Kokai Giho, Kogi No. 2001-1745 (published by Hatsumei Kyokai, March 15, 2001), materials described on pages 17 to 22 are preferably used.

The addition amount of additives is preferably from 0.01 to 20 weight% of the transparent support, more preferably from 0.05 to 10 weight%.

[0115]

A transparent substrate may be subjected to surface treatment. The examples of surface treatments include chemical treatment, mechanical treatment, corona discharge treatment, flame treatment, UV treatment, high frequency treatment, glow discharge treatment, active plasma treatment, laser treatment, mixed acid treatment and ozone oxidation treatment. Specifically, the contents in Hatsumei Kyokai Kokai Giho Kogi No. 2001-1745 (published on March 15, 2001),

pp. 30 and 31, and JP-A-2001-9973 are exemplified. The preferred surface treatments are glow discharge treatment, UV treatment, corona discharge treatment and flame treatment, and more preferred treatments are glow discharge treatment and UV treatment.

[0116]

In the antireflection film of the invention, an inorganic filler is preferably added to the constitutive layers for the purpose of increasing the film strength. The inorganic filler to be added to the constitutive layers may be the same or different in the layers, and it is desirable that the type and the amount of the filler to be added to the layers are varied in accordance with the necessary properties including the refractive index, the film strength, the thickness and the coatability of the constitutive layers. Although not specifically limited, the shape of the inorganic filler for use in the invention may be any one, for example, including spherical, tabular, fibrous, rod, amorphous or hollow structures. Any of these structures are preferred in the invention, but spherical fillers are more preferred as their dispersibility is good. The type of the inorganic filler is not also specifically defined. However, amorphous fillers are preferred. For example, metal oxides, nitrides, sulfides or halides are preferred; and metal oxides are more preferred.

[0117]

The metal atom of the metal oxides includes Na, K, Mg, Ca, Ba, Al, Zn, Fe, Cu, Ti, Sn, In, W, Y, Sb, Mn, Ga, V, Nb, Ta, Ag, Si, B, Bi, Mo, Ce, Cd, Be, Pb and Ni. For obtaining transparent cured films, the mean particle size of the inorganic filler is preferably from 0.001 to 0.2 μm , more preferably from 0.001 to 0.1 μm , even more preferably from 0.001 to 0.06 μm . The mean particle size of the particles is determined by the use of a Coulter counter. In the invention, the method of using the inorganic filler is not specifically limited. For example, the inorganic filler may be used in dry, or may be used after dispersed in water or in an organic solvent. In the invention, a dispersion stabilizer is preferably used for preventing the aggregation and deposition of the inorganic filler. For the dispersion stabilizer, herein usable are polyvinyl alcohol, polyvinyl pyrrolidone, cellulose derivatives, polyamides, phosphates, polyethers, surfactants, silane coupling agents, titanium coupling agents. In particular, silane coupling agents are preferred as effective for enhancing the strength of the cured films. The amount of the silane coupling agent serving as a dispersion stabilizer is not specifically limited. For example, the amount may be at least 1 part by weight relative to 100 parts by weight of the inorganic filler. The method of adding the dispersion stabilizer is not also specifically defined. For example, the stabilizer may be previously hydrolyzed before it is added to the system, or the silane coupling agent

serving as a dispersion stabilizer may be mixed with an inorganic filler and then it may be hydrolyzed and condensed. Of the two, the latter is preferred. The inorganic filler to be added to the constitutive layers will be described hereinunder.

[0118]

[Hard-coat layer]

The hard-coat layer of the antireflection film of the invention is described below.

The hard-coat layer includes a binder which is to impart a hard coat property to the layer, optionally mat particles which are to impart an antiglare property thereto, and an inorganic filler which is for making the layer have a high refractive index, for preventing the layer from being shrunk after crosslinking, and for increasing the mechanical strength of the layer. The binder is preferably a polymer having a saturated hydrocarbon chain or a polyether chain as the backbone structure thereof, more preferably a polymer having a saturated hydrocarbon chain as the backbone structure thereof. Also preferably, the binder polymer has a crosslinked structure. The binder polymer having a saturated hydrocarbon chain as the backbone structure thereof is preferably a polymer of an ethylenic unsaturated monomer. The binder polymer having a saturated hydrocarbon chain as the backbone structure thereof and having a crosslinked structure is preferably a (co)polymer of a monomer having at

least two ethylenic unsaturated groups. For forming a high-refractive index layer, it is desirable that the monomer structure for the polymer contains an aromatic ring, and at least one atom selected from halogen atoms except fluorine, and sulfur atom, phosphorus atom and nitrogen atom.

[0119]

The monomer having at least two ethylenic unsaturated groups includes esters of polyalcohols and (meth)acrylic acid (e.g., ethylene glycol di(meth)acrylate, 1,4-cyclohexane diacrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, pentaerythritol hexa(meth)acrylate, 1,3,5-cyclohexanetriol triacrylate, polyurethane polyacrylate, polyester polyacrylate), vinylbenzene and its derivatives (e.g., 1,4-divinylbenzene, 4-vinylbenzoic acid-2-acryloyl ethyl ester, 1,4-divinylcyclohexanone), vinyl sulfones (e.g., divinyl sulfone), acrylamides (e.g., methylenebisacrylamide), and methacrylamides.

[0120]

Specific examples of the high-refractive index monomer are bis(4-methacryloylthiophenyl) sulfide, vinyl naphthalene, vinylphenyl sulfide, 4-methacryloxyphenyl-4'-methoxyphenyl thioether.

[0121]

The polymerization of the ethylenic unsaturated group-having monomer may be effected through exposure to active energy rays or heat in the presence of a photoradical polymerization initiator or a thermal radical polymerization initiator.

Accordingly, a coating liquid that contains an ethylenic unsaturated group-having monomer, a photoradical initiator or a thermal radical initiator, mat particles and an inorganic filler is prepared, and this is applied onto a transparent support and then polymerized and cured through exposure to active energy rays or heat to form an antireflection film.

[0122]

The polymer having a polyether structure as the backbone structure thereof is preferably a ring-opened polymer of a polyfunctional epoxy compound. The ring-opening polymerization of the polyfunctional epoxy compound may be effected through exposure to active energy rays or heat in the presence of an optical acid generator or a thermal acid generator. Accordingly, a coating liquid that contains a polyfunctional epoxy compound, an optical acid generator or a thermal acid generator, mat particles and an inorganic filler is prepared, and this is applied onto a transparent support and then polymerized and cured through exposure to active energy rays or heat to form an antireflection film.

[0123]

In place of or in addition to the monomer that has at least two ethylenic unsaturated groups, a crosslinking functional group-having monomer may be used so as to introduce a crosslinking functional group into the polymer, and the crosslinking functional group is reacted to thereby introduce a crosslinked structure into the binder polymer. Examples of the crosslinking functional group include an isocyanate group, an epoxy group, an aziridine group, an oxazoline group, an aldehyde group, a carbonyl group, a hydrazine group, a carboxyl group, a methylol group and an active methylene group. Vinyl sulfonic acids, acid anhydrides, cyanoacrylate derivatives, melamines, etherified methylols, esters and urethanes, and metal alkoxides such as tetramethoxysilane may also be used as monomers for introducing a crosslinked structure into the polymer. A functional group that may be crosslinkable as a result of decomposition reaction, such as a blocked isocyanate group may also be used. Accordingly, in the invention, the crosslinking functional group may not be one that is directly reactive, but may be one that becomes reactive as a result of decomposition. The binder polymer having such a crosslinking functional group may be, after applied onto a support, heated to form the intended crosslinked structure.

[0124]

The hard-coat layer may optionally contain mat particles, for example, inorganic compound particles or resin

particles having a mean particle size of from 1 to 10 μm , preferably from 1.5 to 7.0 μm . Specific examples of the mat particles are inorganic compound particles such as silica particles, TiO_2 particles; and resin particles such as crosslinked acrylic particles, crosslinked styrene particles, melamine resin particles, benzoguanamine resin particles. Of those, more preferred are crosslinked styrene particles. Regarding their shape, the mat particles may be either true-spherical or amorphous. Two or more different types of mat particles may be used herein as combined. The amount of the mat particles that may be in the antiglare hard-coat layer formed herein is preferably from 10 to 1,000 mg/m^2 , more preferably from 30 to 100 mg/m^2 . In an especially preferred embodiment of the hard-coat layer, crosslinked styrene particles are used as the mat particles and large crosslinked styrene particles having a particle size of larger than 1/2 of the thickness of the hard-coat layer account for from 40 to 100 % of all the crosslinked styrene particles in the layer. In this, the particle size distribution of the mat particles is determined according to a Coulter counter method, and the thus-determined distribution is converted into a particle number distribution.

[0125]

In addition to the above-mentioned mat particles, the hard-coat layer preferably contains an inorganic filler for further increasing the refractive index of the layer. The

inorganic filler includes an oxide of at least one metal selected from titanium, zirconium, aluminium, indium, zinc, tin and antimony, and has a mean particle size of from 0.001 to 0.2 μm , preferably from 0.001 to 0.1 μm , more preferably from 0.001 to 0.06 μm . Specific examples of the inorganic filler that may be used in the hard-coat layer are TiO_2 , ZrO_2 , Al_2O_3 , In_2O_3 , ZnO , SnO_2 , Sb_2O_3 , ITO. TiO_2 and ZrO_2 are especially preferred in view of their ability to increase the refractive index of the layer. Preferably, the inorganic filler is subjected to surface treatment with a silane coupling agent or a titanium coupling agent. For the treatment, preferably used is a surface-treating agent that may give a functional group capable of reacting with a binder, to the filler surface. The amount of the inorganic filler to be added to the layer is preferably from 10 to 90 %, more preferably from 20 to 80 %, even more preferably from 30 to 75 % of the total weight of the hard-coat layer. Since the filler's particle size is sufficiently smaller than the wavelength of light, the filler does not cause light scattering therearound, and the dispersion formed by dispersing the filler in the binder polymer behaves as an optically uniform substance as a whole.

[0126]

The total refractive index of the mixture of the binder and the inorganic filler in the hard-coat layer in the invention is preferably from 1.57 to 2.00, more preferably

from 1.60 to 1.80. In order to control the refractive index to fall within the range as above, the type of the binder and the inorganic filler and the blend ratio of the two may be suitably selected. How to make the selection can be readily found through previous experiments.

[0127]

Preferably, the thickness of the hard-coat layer is from 1 to 10 μm , more preferably from 1.2 to 6 μm .

[0128]

Thus constructed, the antireflection film of the invention may have a haze value of from 3 to 20 %, preferably from 4 to 15 %, and its mean reflectivity at from 450 to 650 nm may be at most 1.8 %, preferably at most 1.5 %. Having a haze value and a mean reflectivity each falling within the range as above, the antireflection film of the invention realizes good antiglare and antireflection properties not detracting from the transmitted image quality.

[0129]

The polarizing plate of the invention includes the above-described antireflection film which is used in at least one of the two protective films for the polarizing sheet. In the invention, use of the antireflection film on the outermost surface makes it possible to prevent reflection of external light, providing a polarizing plate excellent in scar resistance, dirt resistance and others. Further, in the polarizing plate of the invention an antireflection film may

also be used as a protective film, thereby reducing the production cost.

[0130]

An antireflection film of the invention can be applied to image display devices such as liquid crystal display devices (LCD), plasma display panels (PDP), electroluminescent display devices (ELD), or cathode-ray tube display devices (CRT). Since the antireflection film of the invention has a transparent support, the film is used by adhering the transparent support side to the image display surface of the image display device.

[0131]

In an antireflection film of the invention, when the film is used as one side of surface protection film of the polarizing film, they are preferably applicable to transmissive type, reflective-type and semi-transmissive type liquid crystal display devices based on modes of twisted nematic (TN), super-twisted nematic (STN), vertical alignment (VA), in-plane switching (IPS), optically compensated bend cell (OCB), and the like.

[0132]

The liquid crystal cell based on VA mode includes (1) liquid crystal cell based on the VA mode in a narrow sense in which rod-like liquid crystal molecules are oriented in a substantially vertical direction when no voltage is applied

and in a substantially horizontal direction when voltage is applied (described in JP-A-2-176625), (2) liquid crystal cell (MVA mode) in which the VA mode is multi-domained for widening the viewing angle [SID97 described in Digest of Tech. Papers (preliminary reports), 28, (1997), 845], (3) liquid crystal cell (n-ASM mode) in which rod-like liquid crystal molecules are oriented in a substantially vertical direction when no voltage is applied and subjected to twisted multi-domain orientation when voltage is applied (described in the preliminary report on the discussion of the Japan Liquid Crystal Society, 58-59 (1998)), and (4) liquid crystal cell based on SURVAIVAL mode (published in the LCD International 98).

[0133]

The liquid crystal cell based on the OCB mode is a liquid crystal cell based on bend orientation mode in which rod-like liquid crystal molecules are oriented in a substantially opposite direction (symmetrical) between the upper and lower part of the liquid crystal cell. The liquid crystal display device using the liquid crystal cell based on bend orientation mode has been disclosed in the specification of USP No. 4583825 or USP No. 5410422. Since rod-like liquid crystal molecules are oriented symmetrically between the upper and lower parts of the liquid crystal cell, the liquid crystal cell of the bend orientation mode is provided with self optical compensation function. Therefore, this liquid

crystal mode is also called OCB (optical compensation bend) liquid crystal mode. The liquid crystal display device based on bend orientation mode has an advantage of high response speed.

[0134]

In the liquid crystal cell based on the ECB mode, the rod-like liquid crystal molecules are oriented in a substantially horizontal direction when no voltage is applied. As it is the most used as a color TFT liquid crystal display device, there are descriptions in many documents. For example, EL, PDP, and LCD Display published by Toray Research Center (2001), and the like, describes them.

[0135]

Particularly, in terms of the liquid crystal display device of TN mode and IPS mode, as described in JP-A-2001-1000043 and the like, an optical compensation film having viewing angle magnification effect is disposed to the surface of opposite side of antireflective film of the invention within two protection films on the inside and the outside of the polarizing film. Therefore, a polarizing plate can be obtained having an antireflection effect and viewing angle magnification effect with the thickness of one polarizing plate, and particularly is preferable.

[Examples]

[0136]

The invention will be explained in detail by referring

to the following examples. However, it shall be construed that the invention is not limited to these examples. Parts and percentages are based on weight, unless otherwise specified.

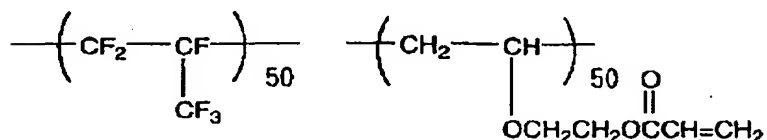
[0137]

(Synthesis of perfluoroolefin copolymer (1))

[0138]

[CHEM. 12]

Perfluoroolefin copolymer (1)



(50:50 indicates mole ratio)

[0139]

Ethyl acetate, 40 ml; hydroxyethyl vinyl ether, 14.7 g; and dilauroyl peroxide, 0.55 g, were fed into a 100 ml-capacity stainless steel autoclave equipped with an agitator, and any air remaining in the system was expelled and replaced with nitrogen gas. Further, hexafluoropropylene (HFP), 25 g, was fed into the autoclave, and the temperature was elevated up to 65°C. The pressure was 5.4 kg/cm² when the temperature in the autoclave reached 65°C. The temperature was maintained to continue the reaction for 8 hours, and heating was discontinued at the time the pressure went down to 3.2 kg/cm², and then cooled. When the temperature inside the autoclave was lowered to room temperature, unreacted monomers

were expelled to collect the reaction liquid by opening the autoclave. Thus the obtained reaction liquid was fed into an excessive quantity of hexane, and solvents were removed by decantation to collect a deposited polymer. Further, the polymer was dissolved in a small quantity of ethyl acetate to effect hexane precipitation twice, thereby completely removing remaining monomers. After drying, the polymer, 28 g, was obtained. Then, the polymer, 20 g, was dissolved in N,N-dimethyl acetamide, 100 ml, to which acrylic acid chloride, 11.4g, was dropped, with ice used for cooling, and the reaction liquid was agitated for 10 hours at room temperature. Ethyl acetate was added to the reaction liquid, washed with water and concentrated after extraction of organic layers. Thus the obtained polymer was precipitated again with hexane to yield 19 g of perfluoroolefin copolymer (1). The polymer was 1.421 in the refractive index.

[0140]

(Preparation of sol solution a)

Methyl ethyl ketone, 120 parts, acryloyloxypropyl trimethoxy silane (KBM-5103 made by Shin-Etsu Chemical Co., Ltd.), 100 parts, diisopropoxy aluminum ethyl, 3 parts, were added to a reaction vessel equipped with an agitator and a reflux condenser, and mixed. Then, ion-exchanged water, 30 parts, was added and the resultant was allowed to react at 60°C for 4 hours, and cooled down to room temperature to obtain a sol solution a. The weight-average molecular weight

was 1600, and of compounds higher than oligomer compounds, the compounds with molecular weight from 1,000 to 20,000 were 100 %. Gas chromatography revealed that acryloyloxypropyl trimethoxy silane of the raw materials did not remain at all.

[0141]

(Preparation of coating solution A for hard-coat layer)

PETA	50.0 parts by weight	
Irgacure 184	2.0 parts by weight	
SX-350 (30 %)	1.7 parts by weight	
Crossed acryl/styrene particles (30 %)		13.3

parts by weight

FP-132	0.75 parts by weight	
KBM-5103	10.0 parts by weight	
Toluene	38.5 parts by weight	

[0142]

(Preparation of coating solution B for hard-coat layer)

Desolite Z7404	100 parts by weight	
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(Zirconia fine particles-containing hard-coat compound solution, made by JSR)

DPHA (UV cure resin: Nippon Kayaku Co., Ltd.)

31 parts by weight

KBM-5103	10 parts by weight	
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KE-P150	8.9 parts by weight	
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(1.5 μ m silica particles: Nippon Shokubai Co., Ltd.)

MXS-300	3.4 parts by weight	
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(3 μ m cross-linked PMMA particles: Soken Chemical &

Engineering Co., Ltd.)

MEK (methyl ethyl ketone) 29
parts by weight

MIBK (methyl isobutyl ketone) 13
parts by weight

[0143]

(Preparation of coating solution C for hard-coat layer)

Poly (glycygyl methacrylate) of weight-average molecular weight 15,000, 270.0 parts by weight, methyl ethyl ketone, 730.0 parts by weight, cyclohexanone 500.0 parts by weight and photo polymerization initiator (Irgacure 184, Ciba Specialty Chemicals) 50.0 parts by weight were added to trimethylolpropane triacrylate (TMPTA: Viscoat # 295, Nippon Kayaku Co., Ltd.), 750.0 parts by weight, and mixed.

[0144]

The above-described coating solutions A and B were filtered through a polypropylene filter with a pore size of 30 μm , and the solution C was filtered through a polypropylene filter with a pore size of 0.4 μm to prepare the respective coating solutions for hard-coat layers.

[0145]

(Preparation of titanium dioxide fine particles dispersing solution)

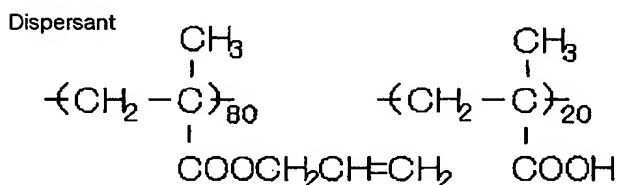
Titanium dioxide fine particles (MPT-129C, Ishihara Sangyo Kaisha Ltd. $\text{TiO}_2\text{:Co}_3\text{O}_4\text{:Al}_2\text{O}_3\text{:ZrO}_2$ =90.5:3.0:4.0:0.5 weight ratio) which contained cobalt and received surface-

treatment with aluminum hydroxide and zirconium hydroxide was used as titanium dioxide fine particles.

The following dispersant 41.1 parts by weight and cyclohexanone 701.8 parts by weight were added to the above-described particles 257.1 parts by weight, and the resultant was dispersed by using a dyno mill to prepare a titanium dioxide dispersing solution with a weight mean diameter of 70 nm.

[0146]

Dispersant



[CHEM. 13]

[0147]

(Preparation of coating solution A for middle-refractive index layer)

A mixture of dipentaerythritol pentaacrylate and dipentaerythritol hexaacrylate (DPHA), 68.0 parts by weight; photo polymerization initiator (Irgacure 907, Ciba Specialty Chemicals), 3.6 parts by weight; photo sensitizer (Kayacure-DETX, Nippon Kayaku Co., Ltd.), 1.2 parts by weight; methyl ethyl ketone, 279.6 parts by weight and cyclohexanone, 1049.0 parts by weight were added to the above-described titanium dioxide dispersing solution, 99.1 parts by weight and

agitated. After a sufficient agitation, the resultant was filtered through a polypropylene filter with a pore size of 0.4 μ m.

[0148]

(Preparation of coating solution A for high-refractive index layer)

A mixture of dipentaerythritol penta acrylate and dipentaerythritol hexaacrylate (DPHA, Nippon Kayaku Co., Ltd.), 40.0 parts by weight; photo polymerization initiator (Irgacure 907, Ciba Specialty Chemicals), 3.3 parts by weight; photo sensitizer (Kayacure-DETX, Nippon Kayaku Co., Ltd.), 1.1 parts by weight; methyl ethyl ketone, 526.2 parts by weight; and cyclohexanone, 459.6 parts by weight, were added to the above-described titanium dioxide dispersing solution A, 469.8 parts by weight, and agitated. The resultant was filtered through a polypropylene filter with a pore size of 0.4 μ m.

[0149]

(Preparation of coating solution A for low-refractive index layer)

DPHA	4.0 parts by weight
Hollow silica (18.2 %)	40.0 parts by weight
Irgacure 907	0.2 parts by weight
Sol solution a	6.2 parts by weight
MEK	299.6 parts by weight

[0150]

(Preparation of coating solution B for low-refractive index layer)

DPHA	3.3 parts by weight
Hollow silica (18.2 %)	40.0 parts by weight
RMS-033	0.7 parts by weight
Irgacure 907	0.2 parts by weight
Sol solution a	6.2 parts by weight
MEK	299.6 parts by weight

[0151]

(Preparation of coating solution C for low-refractive index layer)

JTA113 (6 %)	13.0 parts by weight
MEK-ST-L	1.3 parts by weight
Sol solution a	0.6 parts by weight
MEK	5.0 parts by weight
Cyclohexanone	0.6 parts by weight

[0152]

(Preparation of coating solution D for low-refractive index layer)

JN7228A (6 %)	13.0 parts by weight
MEK-ST-L	1.3 parts by weight
Sol solution a	0.6 parts by weight
MEK	5.0 parts by weight
Cyclohexanone	0.6 parts by weight

[0153]

(Preparation for coating solution E for low-refractive index

layer)

JN7228A (6 %)	100.0 parts by weight
MEK-ST	4.3 parts by weight
MEK-ST-L	5.1 parts by weight
Sol solution a	2.2 parts by weight
MEK	15.0 parts by weight
Cyclohexanone	3.6 parts by weight

[0154]

(Preparation of coating solution F for low-refractive index layer)

Exemplified compound; P-1	14.0 parts by weight
X-22-164C	0.42 parts by weight
Irgacure 907	0.7 parts by weight
MIBK	84.7 parts by weight

[0155]

(Preparation of coating solution G for low-refractive index layer)

Tetramethoxy silane, 30 parts by weight, and methanol, 240 parts by weight, were put into a four-neck reaction flask and agitated, with solution temperature maintained at 30°C, to which a solution prepared by adding nitric acid, 2 parts by weight, to water, 6 parts by weight, was added, the resultant was agitated at 30°C for 5 hours to obtain an alcohol solution (solution A) of siloxane oligomer. The siloxane oligomer was subjected to GPC, finding that the relative molecular weight was 950 on conversion to ethylene

glycol/polyethylene oxide.

[0156]

In separate procedures, methanol, 300 parts by weight, was added to a four-neck reaction flask and then oxalic acid, 30 parts by weight, was mixed with agitation. Thus the prepared solution was heated while refluxing, to which tetramethoxy silane, 30 parts by weight, and tridecafluorooctyl trimethoxy silane, 8 parts by weight, were added. The resultant was heated for 5 hours while refluxing, and cooled to obtain a fluorine compound solution (solution B) having a fluoroalkyl structure and polysiloxane structure.

[0157]

Solution A, 30 parts by weight, and solution B, 100 parts by weight, were mixed and diluted with butyl acetate so that the dry-solid based concentration in a coating mixture solution was 1 % by weight to obtain coating solution G for low-refractive index layer.

[0158]

(Preparation of coating solution H for a low-refractive index layer)

Solution A and solution B were prepared similarly as with coating solution G for a low-refractive index layer, and polydimethyl siloxane DMS-H21 with a hydrogen terminal group (made by Gelest), 1 weight part, and hollow silica particles (18.2 %) to be described later, 80 parts by weight, were added to solution A, 30 parts by weight, and solution B, 100

parts by weight, and mixed. The resultant was diluted with butyl acetate so that the dry-solid based concentration in a coating mixture solution was 1 % by weight to obtain coating solution H for a low-refractive index layer.

[0159]

The above-described solution was agitated and then filtered through a polypropylene filter with pore size of 1 μ m to prepare the coating solution for low-refractive index layer.

[0160]

The following are other compounds (those omitted for detailed explanation in the text) used in the invention.

PETA: mixture of pentaerythritol triacrylate with pentaerythritol tetraacrylate (made by Nippon Kayaku Co., Ltd.)

Irgacure 184: polymerization initiator (made by Ciba Specialty Chemicals)

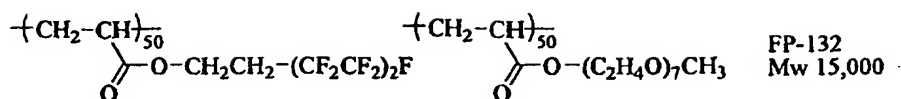
SX-350: cross-linked polystyrene particles with a mean particle size of 3.5 μ m (refractive index. 1.60, made by Soken Chemical & Engineering Co., Ltd., 30 % toluene dispersing solution, to be used after dispersion at 10,000 rpm for 20 minutes by Polytron dispersing equipment)

Cross acryl/styrene particles: mean particle size of 3.5 μ m (refractive index 1.55, made by Soken Chemical & Engineering Co., Ltd., 30 % toluene dispersing solution)

FP-132: fluorine surface modifier

[0161]

[CHEM. 14]



[0162]

KBM-5103: silane coupling agent (made by Shin-Etsu Chemical Co., Ltd.)

JN-7228A: thermal crosslinking fluorine-containing polymer (refractive index, 1.42; dry solid based concentration, 6 %; made by JSR), trade name: Opstar JN-7228A

JTA-113: thermal crosslinking fluorine-containing polymer (refractive index, 1.44; dry solid based concentration, 6 %; made by JSR), trade name: Opstar JTA-113

P-1: perfluoroolefin copolymer (1)

DPHA: mixture of dipentaerythritol pentaacrylate with dipentaerythritol hexaacrylate (Nippon Kayaku Co., Ltd.)

MEK-ST-L: silica sol (silica, MEK-ST with different particle size; mean particle size, 45 nm; dry solid based concentration, 30 %; made by Nissan Chemical Industries Ltd.)

Hollow silica: KBM-5103 surface-modified hollow silica sol (silica in relation to surface-modified, 30 % parts by weight; refractive index, 1.31; mean particle size, 60 nm; solid based concentration, 18.2 %)

KF96-1000CS: straight silicone (made by Shin-Etsu Chemical Co., Ltd.)

X22-164C: reactive silicone (made by Shin-Etsu Chemical

Co., Ltd.)

RMS-033: reactive silicone (made by Gelest)

R-2020: fluoroalkyl acrylate monomer (made by Daikin Industries Ltd.)

R-3833: fluoroalkyl acrylate monomer (made by Daikin Industries Ltd.)

FMS-121: fluoroalkyl silicone (made by Gelest)

Irgacure 907: photo polymerization initiator (made by Ciba Specialty Chemicals)

[0163]

[Example 1]

(1-1) Coating of hard-coat layer A and hard-coat layer C

Triacetyl cellulose film (TD80U made by Fuji Photo Film Co., Ltd.) was wound out as a support in a roll form, on which the above-described coating solution for the hard-coat layer was directly coated by using a micro gravure roll of 50 mm in diameter having the gravure pattern of 180 lines per inch and 40 μm in depth and a doctor blade at a transfer speed of 30 m/minute, dried at 60°C for 150 seconds, then, an air-cooled metal halide lamp (made by Eye Graphics Co., Ltd.) (160W/cm) was used to radiate ultraviolet rays at a brightness of 400 mW/cm^2 , with radiation of 250 mJ/cm^2 for hard-coat layer A and 300 mJ/cm^2 for the hard-coat layer C, under nitrogen purge, thereby curing the coated layer to form a hard-coat layer, which was then wound up. After curing,

the number of rotations of the gravure roll was adjusted so that the hard-coat layer A was given a thickness of 6 μm and the hard-coat layer C was given a thickness of 8 μm .

[0164]

(1-2) Coating of hard-coat layer B

Triacetyl cellulose film (TD80U made by Fuji Photo Film Co., Ltd.) was wound out as a support in a roll form, on which the above-described coating solution for the hard-coat layer was directly coated by using a micro gravure roll of 50 mm in diameter having the gravure pattern of 135 lines per inch and 60 μm in depth and a doctor blade at a transfer speed of 10m/minute, dried at 60°C for 150 seconds, then, an air-cooled metal halide lamp (made by Eye Graphics Co., Ltd.) (160 W/cm) was used to radiate ultraviolet rays at a brightness of 400 mW/cm², with radiation of 250 mJ/cm², under nitrogen purge, thereby curing the coated layer to form a hard-coat layer, which was then wound up. After curing, the number of rotations of the gravure roll was adjusted so that the hard-coat layer was given a thickness of 3.6 μm .

[0165]

(2) Coating of middle-refractive index layer A

Triacetyl cellulose film (TD-80UF made by Fuji Photo Film Co., Ltd.) in which coating was given up to the hard-coat layer was wound out again, on which the coating solution for the middle-refractive index layer was coated by using a micro gravure roll of 50 mm in diameter having the gravure

pattern of 180 lines per inch and 40 μm in depth and a doctor blade. The drying process was conducted at 90°C for 30 seconds and an air-cooled metal halide lamp (made by Eye Graphics Co., Ltd.) (180 W/cm) was used to radiate ultraviolet rays at a brightness of 400 mW/cm^2 , with radiation of 400 mJ/cm^2 , under nitrogen purge so as to give an oxygen concentration of 1.0 % or less by volume. The number of rotations of gravure roll was adjusted so as to give 67 nm in thickness after coating, thereby providing the middle-refractive index layer, which was then wound up. The middle-refractive index layer after curing was 1.630 in the refractive index.

[0166]

(3) Coating of high-refractive index layer A.

Triacetyl cellulose film (TD-80UF made by Fuji Photo Film Co., Ltd.) in which coating was given up to the middle-refractive index layer was wound out again, on which the coating solution for the high-refractive index layer was coated by using a micro gravure roll of 50 mm in diameter having the gravure pattern of 180 lines per inch and 40 μm in depth and a doctor blade. The drying process was conducted at 90°C for 30 seconds and an air-cooled metal halide lamp (made by Eye Graphics Co., Ltd.) (240 W/cm) was used to radiate ultraviolet rays at a brightness of 600 mW/cm^2 , with radiation of 400 mJ/cm^2 , under nitrogen purge so as to give an oxygen concentration of 1.0 % or less by volume. The

number of rotations of gravure roll was adjusted so as to give 107 nm in thickness after coating, thereby providing the high-refractive index layer, which was then wound up. The high-refractive index layer after curing had a refractive index of 1.905.

[0167]

(4-1) Coating of low-refractive index layer [coating and curing process A]

Triacetyl cellulose film in which coating was given up to the hard-coat layer or the high-refractive index layer was wound out again, on which the coating solution for the above-described low-refractive index layer was coated by using a micro gravure roll of 50 mm in diameter having the gravure pattern of 180 lines per inch and 40 μm in depth and a doctor blade, at a transfer speed of 15 m/minute, and a preliminary drying was conducted at 120°C for 150 seconds and a secondary drying was conducted at 140°C for 8 minutes. Then, an air-cooled metal halide lamp (made by Eye Graphics Co., Ltd.) (240 W/cm) was used to radiate ultraviolet rays at a brightness of 400 mW/cm², with radiation of 900 mJ/cm², under nitrogen purge. The number of rotations of the gravure roll was adjusted so as to give 100 nm in thickness, thereby providing the low-refractive index layer, which was then wound up.

[0168]

(4-2) Coating of low-refractive index layer [coating

and curing process B]

Coating of the low-refractive index layer was conducted similarly as in [coating and curing process A] except that the secondary drying was not performed.

[0169]

(4-3) Coating of low-refractive index layer [coating and curing process C]

A wire bar was used to coat the coating solution for the low-refractive index layer prepared above so as to give thickness of about 100 nm after curing, and the resultant was subjected to heat curing at 90°C for 1 hour to form an antireflection layer.

[0170]

(4-4) Coating of low-refractive index layer [coating and curing process D]

Triacetyl cellulose film which was coated up to the hard-coat layer was wound out again, on which the coating solution for the above-described low-refractive index layer was coated by a die coating method. After the resultant was dried at 120°C for 150 seconds and then at 140°C for 8 minutes, an air-cooled metal halide lamp (made by Eye Graphics Co., Ltd.) of 240 W/cm was used to radiate ultraviolet rays at a brightness of 400 mW/cm², with radiation of 900 mJ/cm², under nitrogen purge. The low-refractive index layer of 100 nm in thickness was formed, which was then wound up.

[0171]

(Preparation of antireflection film samples)

As shown in Tables 1 to 3, antireflection film samples were prepared according to the above-described method.

[0172]

[Table 1]

Sample No.	Low-refractive index layer					Hard-coat layer	Remarks
	Coating solution	Changes from original coating solution	Hollow silica particles	Surface energy lowering compound/binder	Coating and curing method		
001	C	None	Absent	Present	A	A	Comparative Example
002	A	None	Present	Absent	B	A	Comparative Example
003	B	None	Present	Present	B	A	Present Invention
004	B	Change from RMS-033 to X22-164C on equal weight basis	Present	Present	B	A	Present Invention
005	B	Change from RMS-033 to KF96-1000CS on equal weight basis	Present	Present	B	A	Present Invention
006	B	Change from RMS-033 to FMS121 on equal weight basis	Present	Present	B	A	Present Invention
007	B	RMS-033 =0.35 parts by weight, DPHA =3.65 parts by weight	Present	Present	B	A	Present Invention
008	A	R-2020 =1.0 parts by weight added, DPHA =3.0 parts by weight	Present	Present	B	A	Present Invention
009	A	R-3833 =1.6 parts by weight added, DPHA =2.4 parts by weight	Present	Present	B	A	Present Invention
010	B	PHA =5.8 parts by weight, sol solution a excluded, MEK =295.9 parts by weight	Present	Present	B	A	Present Invention
011	B	R-2020 =0.83 parts by weight added, DPHA =2.47 parts by weight	Present	Present	B	A	Present Invention
012	B	None	Present	Present	D	A	Present Invention
013	D	None	Absent	Present	A	A	Comparative Example

[0173]
[Table 2]

Sample No.	Low-refractive index layer						Hard-coat layer	Remarks
	Coating solution	Changes from original coating solution	Hollow silica particles	Surface free energy lowering compound/binder	Coating and curing method			
101	G	None		Absent	Absent	C	A	Comparative Example
102	H	None		Present	Present	C	A	Present Invention
103	A		DPHA =0 parts by weight, JTA113 (6 %) =66.7 parts by weight, MEK =236.9 parts by weight	Present	Present	A	A	Present Invention
104	A		DPHA =0 parts by weight, exemplified compound; P-1 =4.0 parts by weight	Present	Present	B	A	Present Invention
105	A		DPHA =0.8 parts by weight, exemplified compound; P-1 =3.2 parts by weight	Present	Present	B	A	Present Invention
106	B		DPHA =0.7 parts by weight, exemplified compound; P-1 =2.6 parts by weight	Present	Present	B	A	Present Invention
107	B		DPHA =0.7 parts by weight, exemplified compound; P-20 =2.6 parts by weight	Present	Present	B	A	Present Invention
108	B		DPHA =0.7 parts by weight, exemplified compound; P-3 =2.6 parts by weight	Present	Present	B	A	Present Invention
109	B		DPHA =0.7 parts by weight, exemplified compound; P-1 =2.6 parts by weight	Present	Present	D	A	Present Invention

[0174]
[Table 3]

Sample No.	Low-refractive index layer					High-refractive index layer	Middle-refractive index layer	Hard-coat layer	Remarks
	Coating solution	Hollow silica particles	Surface energy compound/binder	free lowering	Coating and curing method				
201	E	Absent	Present		A	Absent	Absent	B	Comparative Example
202	B	Present	Present		B	Absent	Absent	B	Present Invention
203	Similar to that for preparing the sample 011	Present	Present		B	Absent	Absent	B	Present Invention
204	Similar to that for preparing the sample 106	Present	Present		B	Absent	Absent	B	Present Invention
205	F	Absent	Present		B	A	A	C	Comparative Example
206	B	Present	Present		B	A	A	C	Present Invention
207	Similar to that for preparing the sample 011	Present	Present		B	A	A	C	Present Invention
208	Similar to that for preparing the sample 106	Present	Present		B	A	A	C	Present Invention

[0175]

(Saponification of antireflection film)

After the film was formed, the following treatments were given to the samples excluding the samples 101 and 102.

Sodium hydroxide solution, 1.5 mol/l, was prepared and maintained at 55°C. Diluted sulphuric acid solution, 0.01 mol/l, was prepared and maintained at 35°C. The prepared antireflection film was immersed into the above-described the sodium hydroxide for 2 minutes and then immersed into water to completely wash away sodium hydroxide solution. After being immersed into the above-described diluted sulphuric acid solution for one minute, the film samples were immersed into water to completely wash away the diluted sulphuric acid solution. Finally, the samples were dried completely at 120°C.

[0176]

(Evaluation of antireflection film)

The film samples obtained after the saponification were evaluated for the following items, however, the samples 101 and 102 were saponification-free samples and evaluated for the following items.

(1) Mean reflectivity ratio

A spectrophotometer (made by JASCO) was used to determine the spectral reflectivity ratio at an incident

angle of 5° in a wavelength range of 380 to 780 nm. The result was used to calculate the mean reflectivity ratio in a wavelength range of 450 to 650 nm.

(2) Evaluation of steel wool scratch resistance

A rubbing tester was used to perform rubbing tests under the following conditions.

Conditions: 25°C , 60 % RH

Material to be rubbed: steel wool (Gerede No. 0000 made by Nihon Steel Wool Co., Ltd.) was wrapped around the rubbing tip of the tester coming into contact with samples (1 cm x 1 cm) and fixed with a band.

Moving distance (one way): 13 cm

Rubbing speed: 13 cm/second

Load: 500 g/cm^2

Tip contacting area: 1 cm x 1 cm

Rubbing times: 10 reciprocating movements

Oil-based black ink was applied on the back of the rubbed material, and observed macroscopically under reflected light to evaluate the rubbed part on the basis of the following criteria.

AA: no scratching at all was found after very careful observation

A: slight and subtle scratching was found after very careful observation

AB: slight scratching was found

B: moderate scratching was found

BC to C: scratching was found at one glance

[0177]

(3) Evaluation of adhesiveness

A utility knife was used to cut 11 vertical lines and 11 horizontal lines on the surface of the antireflection film having the low-refractive index layer, thereby making a total of 100 squares. Polyester adhesive tape (No.31B) made by Nitto Denko Co., Ltd. was pressed to conduct adhesive tests at the same spots 3 times repeatedly. Whether the tape was peeled or not was macroscopically observed to make the following 4-stage evaluation.

AA: of the 100 squares, no peeling was found at all

A: of the 100 squares, less than two squares were peeled

B: of the 100 squares, 3 to 10 squares were peeled

C: of the 100 squares, more than 10 squares were peeled

[0178]

(4) Rubber eraser friction resistance

The antireflection film was fixed on the surface of a glass plate with an adhesive, a rubber eraser MONO (trade name, made by Tombo Pencil Co., Ltd.) hollowed with an 8 mm in diameter and 4 mm in thickness was used as a

head of a friction tester, namely, the rubber eraser was pressed vertically from above on the surface of the antireflection film under a load of 500 g/cm², then, subjected to 200 time-reciprocating friction movements at a stroke length of 3.5 cm and at friction speed of 1.8 cm/s at 25°C and 60 RH %. Thereafter, the rubber eraser was removed and friction parts of samples were macroscopically confirmed. The test was repeated 3 times, and the results were averaged to make the following 4-stage evaluation.

A: scratching was hardly found

B: slight scratching was found

C: clear scratching was found

CC: scratching was found on a whole surface

[0179]

(5) Felt pen wiping performance

The antireflection film was fixed on the surface of a glass plate with an adhesive, and a circle of 5 mm in diameter was drawn 3 times with a tip of a black ink felt pen "Makky Gokuboso (trade name, made by ZEBRA)" at 25°C and 60 RH %. After 5 seconds, a cloth Vencot (trade name, made by Asahi Chemical Industry Co., Ltd.) folded 10 times was used to wipe the circle 20 times in a reciprocating fashion with such a load that a bundle of Vencot was bent. The above-described procedures of drawing the circle and

wiping it were repeated under the same conditions until the circle drawn with the felt pen could no longer be erased after being wiped to count how many times the circle was successfully wiped. The above-described test was repeated 4 times and the results were averaged to make the following 4-stage evaluation.

A: the circle was wiped more than 10 times

B: the circle was wiped several times to less than 10 times

C: the circle was wiped only once

CC: the circle was not wiped at any time

[0180]

(6) Evaluation of surface segregation of silicone (Si atom) and fluoroalkyl (F atom)

ESCA-3400 (made by Shimadzu Corp.) was used to determine the intensity ratio of the photoelectron spectrum, Si2p/C1s (=Si(a)) to F1s/C1s(=F(a)) of Si2p, F1s and C1s on the outer-most surface of individual antireflection films under the conditions (degree of vacuum, 1×10^{-5} Pa; X ray source, target Mg; voltage, 12 kV; current, 20 mA) and the intensity ratio of photoelectron spectrum, Si2p/C1s(=Si(b)) to F1s/C1s(=F(a)) at the lower layer 80 % downward from the surface of the low-refractive index layer ground down to $1/5 (\pm 5 \%)$ of the thickness by using an ion etching equipment attached to the ESCA-3400

(ion gun; voltage, 2 kV; current, 20 mA), from which variation in the intensity ratio, $\text{Si(a)}/\text{Si(b)}$ and $\text{F(a)}/\text{F(b)}$, before and after etching was determined. Then, the following 3-stage evaluation was made on the basis of the individual variations in $\text{Si2p}/\text{Cl1s}$ ratio and $\text{F1s}/\text{Cl1s}$ ratio before and after etching (variation in the intensity ratio of the photoelectron spectrum at the outer-most surface of the low-refractive index layer/intensity ratio of the photoelectron spectrum at the lower layer 80 % downward from the surface of the low-refractive index layer). The above-described determination was made at 3 sites at least 2 cm apart from each other on the same film.

AA: intensity ratio after etching was increased more than 5 times at more than 1 site

A: intensity ratio after etching was increased less than 5 times and more than 3 times at more than 1 site

B: intensity ratio after etching was increased less than 3 to more than 1.5 times at more than 1 site

-: intensity ratio after etching was increased less than 1.5 times or

F1s and Cl1s were determined for intensity at the peak of the respective photoelectron spectra. Si2p was determined for intensity at the peak derived from silicone (Si atom of polydimethylsiloxane) around 105 eV of binding energy, which was used for calculating the above-described

intensity ratio and made distinct from the Si atom derived from inorganic silica particles. Preliminary tests were performed to gradually grind the surface of the low-refractive index layer under different etching conditions, thereby evaluating the etching conditions for reaching the under layer of the hard-coat layer or the high-refractive index layer to such an extent 80 % downward from the surface. The above-described determination was made after preliminary studies.

[0181]

[Table 4]

Sample No.	Mean specular reflectivity (%)	Mean integral reflectivity (%)	Surface free energy : γ_s^v (mN/m)	Rubber eraser friction resistance	Felt wiping performance	Steel wool scratch resistance	Adhesiveness of crosscut	ESCA intensity ratio between upper and lower parts		Remarks
								Si/C	F/C	
001	2.0	2.9	22	B	B	B	A	A	A	Comparative Example
002	1.6	2.6	44	A	C	A	C	-	-	Comparative Example
003	1.6	2.6	21	A	AA	AA	AA	AA	-	Present Invention
004	1.6	2.6	22	A	A	AA	AA	AA	-	Present Invention
005	1.6	2.6	23	A	B	A	AA	AA	-	Present Invention
006	1.6	2.6	23	A	A	A	A	AA	AA	Present Invention
007	1.6	2.6	23	A	A	AA	AA	AA	A	Present Invention
008	1.4	2.4	27	A	B	A	A	-	AA	Present Invention
009	1.4	2.4	30	A	B	A	A	-	AA	Present Invention
010	1.7	2.7	22	B	A	B	B	AA	-	Present Invention
011	1.4	2.4	19	A	AA	AA	AA	AA	AA	Present Invention
012	1.6	2.6	21	A	A	AA	AA	AA	-	Present Invention
013	1.8	2.8	21	CC	AA	B	B	A	A	Comparative Example

[0182]
[Table 5]

Sample No.	Mean specular reflectivity (%)	Mean integral reflectivity (%)	Surface free energy : γ_s^v (mN/m)	Rubber eraser friction resistance	Felt wiping performance	Steel wool scratch resistance	Adhesiveness of crosscut	ESCA intensity ratio between upper and lower parts		Remarks
								Si/C	F/C	

101	1.7	2.7	43	C	C	C	CC	A	A	-	Comparative Example
102	1.5	2.5	25	B	A	AA	B	AA	AA	-	Present Invention
103	1.3	2.3	22	B	AA	A	B	A	A	A	Present Invention
104	1.4	2.4	25	B	B	A	A	A	-	A	Present Invention
105	1.5	2.5	30	A	B	A	A	A	-	A	Present Invention
106	1.5	2.5	22	B	AA	AA	AA	AA	AA	A	Present Invention
107	1.5	2.5	23	B	A	AA	A	AA	AA	A	Present Invention
108	1.5	2.5	22	B	A	AA	A	AA	AA	A	Present Invention
109	1.5	2.5	22	A	A	AA	AA	AA	AA	A	Present Invention

[0183]
[Table 6]

Sample No.	Mean specular reflectivity (%)	Mean integral reflectivity (%)	Surface free energy : γ_{sv} (mN/m)	Rubber eraser friction resistance	Felt wiping performance	Steel wool scratch resistance	Adhesiveness of crosscut	ESCA ratio upper and lower parts		intensity between and lower	Remarks
								Si/C	F/C		
201	1.4	1.9	21	CC	A	C	A	A	A		Comparative Example
202	1.3	1.8	21	A	A	A	AA	AA	-		Present Invention
203	1.3	1.8	19	A	A	A	AA	AA	AA		Present Invention
204	1.4	2.4	22	B	B	A	AA	AA	A		Present Invention
205	0.5	0.5	23	CC	C	B	C	A	A		Comparative Example
206	0.4	0.4	21	A	A	A	AA	AA	-		Present Invention
207	0.4	0.4	20	A	A	A	AA	AA	AA		Present Invention
208	0.4	0.4	22	B	B	A	AA	AA	A		Present Invention

[0184]

The results obtained from Tables 4 to 6 have clearly demonstrated the following.

The antireflection film of the invention has satisfied all the reflectivity ratio, scratch resistance, felt pen wiping performance and adhesiveness to a satisfactory extent, and improved in every respect as an antireflection film. All the samples of the invention attained low reflection, as compared with Sample 001. Samples 003, 008 and 011 prepared by adding silicone and fluoroalkyl compound to Sample 002 improved in felt pen wiping performance. Further, Samples 103 and 106 to which silicone and fluorine are used in combination exhibited a better felt pen wiping performance.

[0185]

[Example 2]

Then, the sample film of the invention described in example 1 was attached to the polarizing plate to prepare a polarizing plate with an antireflection function. Where the polarizing plate was used to prepare a liquid crystal display device in which the antireflection layer was arrayed on the outer-most surface, the device was provided with a smaller reflection of external light, less conspicuous of reflected image and excellent visibility. The device met all the requirements of stain resistance,

dust resistance and film strength which are problems in practical use.

[0186]

[Example 3]

80 μ m-thick triacetyl cellulose film (TAC-TD80U, Fuji Photo Film Co., Ltd.) which was immersed into NaOH solution (1.5 mol/l and 55°C) for 2 minutes, neutralized and washed with water and the triacetyl cellulose film on which the sample of the invention prepared in example 1 was coated were attached to both planes of the polarizing sheet prepared by stretching, after iodine was allowed to adsorb on polyvinyl alcohol, the resultant was then given a protection treatment to prepare a polarizing plate. Thus the prepared polarizing plate was used so that the antireflection film side was arrayed on the outer-most surface in place of the polarizing plate on the observation side used in a liquid crystal display device of a notebook computer equipped with a transmissive-type TN liquid crystal display device (polarization-separating film having a polarization-separating layer (D-BEF made by Sumitomo 3M) was interposed between a backlight and liquid crystal cell). The above-described display device was provided with an extremely small reflection of the background and a quite excellent display quality.

[0187]

[Example 4]

The sample of the invention described in example 1 was attached to the protective film on the liquid crystal cell side of the polarizing plate on the observation side of the transmissive-type TN liquid crystal cell and also to the protective film on the liquid crystal cell of the polarizing plate on the backlight, which were used in the viewing angle widening film (wide-view film SA-12B, made by Fuji Photo Film Co., Ltd.). The above-described constituted liquid crystal display device was provided with an excellent contrast in a bright room, a very wide viewing angle at every respect, quite excellent visibility and a high display quality.

[0188]

[Example 5]

The sample of the invention described in example 1 was attached with an adhesive to the glass plate of an organic EL display device. Such a constituted display device was provided with a lower reflection of the glass surface, a higher visibility and satisfactory stain resistance against finger prints or dust.

[0189]

[Example 6]

The sample of the invention described in example 1 was used to prepare a polarizing plate only one plane of

which was provided an antireflection film, and the $\gamma/4$ plate was attached with the plane opposite side to the plane of the antireflection film-provided polarizing plate, which was attached to the glass plate on an organic EL display device so that the antireflection film was arrayed on the outer-most surface. Such a constituted display device was provided with quite high visibility, with surface reflection and reflection coming inside the surface glass being blocked.

[Brief Description of the Drawing]

[0190]

[Fig. 1] A schematic sectional view illustrating an example of the antireflection film according to the invention.

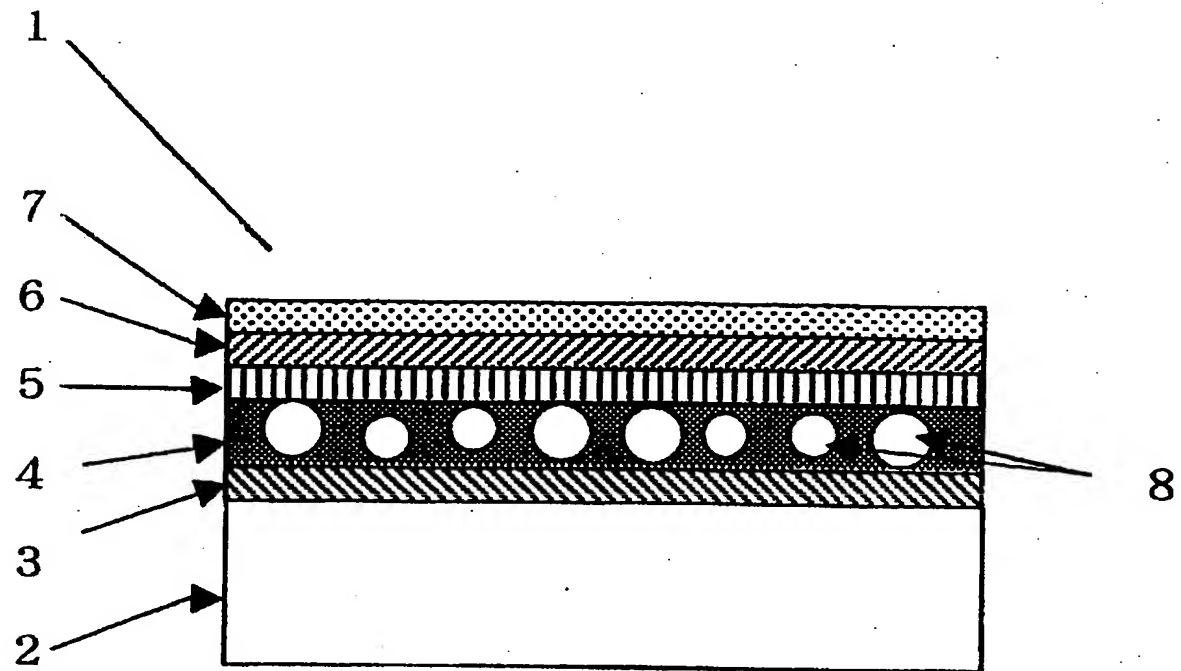
[Brief Description of the Reference Symbols]

[0191]

- 1: Antireflection film
- 2: Transparent support
- 3: Conductive layer
- 4: Hard-coat layer
- 5: Middle-refractive index layer
- 6: High-refractive index layer
- 7: Low-refractive index layer
- 8: Mat particles

[Document Type] Drawing

[FIG. 1]



[Document Type] Abstract

[Abstract]

[Problem to be Solved by the Invention] To provide an antireflection film which is easily and inexpensively producible and which has a good antireflection capability, a good scratch resistance, and a good stain resistance, and has a polarizing plate and a liquid crystal display device utilizing the antireflection film of such excellent ability.

[Means for Solving the Problem] An antireflection film including hollow particles and surface free energy lowering compounds in a low-refractive index layer, a polarizing film and a liquid crystal display device which have the film, wherein the low-refractive index layer is located at the furthest position from the transparent support.

[Selected Drawing] None